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SYSTEMS STUDY OF NITROGEN OXIDE CONTROL METHODS FOR STATIONARY SOURCES

FINAL REPORT - VOLUME II

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FOREWORD

This two-volume report summarizes the results and conclusions of the studies made by Esso Research and Engineering Company for the National Air Pollution Control Administration under Contract No. PH 22-68-55.

Volume I of the report contains the summary of findings, and the 5-year R&D plan recommendations made for NAPCA on the control of nitrogen oxides emissions from stationary sources. The contents of Volume II supplement Volume I with the detailed discussion of the contract study carried out during the period between June 20, 1968 and November 20, 1969.

The systems study of nitrogen oxides control methods for stationary sources was made in the Engineering Research Department of the Government Research Laboratory, managed by Mr. Leonard Berkowitz. Dr. William Bartok was the contractor's project director, and Mr. Alvin Skopp acted as the assistant project director.

The authors wish to acknowledge their indebtedness to the following individuals: Messrs. D. Bruce Henschel and Thomas C. Gilman, the NAPCA project officers for helpful comments; Dr. Chauncey C. Hale for his assistance in making the literature survey; Dr. R. Goldstein for the programming and implementation of the NO kinetic model; Messrs. J. F. Pagel, D. J. Miller, R. C. Petura, and R. Chaneski for process design and cost estimate studies; and other Esso personnel and consultants who provided constructive technical comments. Special thanks are due to the cooperating electric utility companies and petroleum companies for their participation in our industry surveys; to the Babcock and Wilcox Company for their assistance in making cost estimates for combustion equipment; to the American Boiler Manufacturers' Association for providing census data on industrial boilers; and to Foster-Wheeler Corporation and to Combustion Engineering for their expert guidance.

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1. SUMMARY

During the time period between June 20, 1968, and November 20, 1969, Esso Research and Engineering Company has conducted a systems study of nitrogen oxide control methods for stationary sources. This study, funded by the Division of Process Control Engineering of the National Air Pollution Control Administration, represented Phase I of an overall effort sponsored by NAPCA aimed at the control of nitrogen oxide (NO_x) emissions from stationary sources.

The systems study has accomplished three primary goals:

A. Characterization of the stationary NO_x problem for the U.S. by ranking emission sources according to their nature and magnitude, with projections and forecasts of potential NO_x emissions to the year 2000.

B. Assessment of available and potential control technology on the basis of cost effectiveness, in the following broad categories:

- Combustion modification processes, including the definition of requirements for a mathematical model of NO_x formation in fossil fuel combustion processes.
- Removal of NO_x from flue and tail gases by in-process treatment.
- Other industrial process modifications.

C. Development of alternate 5-year plans for NAPCA-sponsored R&D studies aimed at the control of stationary NO_x emissions.

In "problem definition" it has been clearly established that on an uncontrolled basis, the share of stationary sources in NO_x emissions is at least as large as that of mobile sources, or larger. On a nation-wide basis, the estimates show that stationary sources can be expected to contribute 50-60% of the uncontrolled NO_x emissions between the present and the year 2000. The largest single emission source sector is the electric power generating industry, followed by (in decreasing order of importance) intermediate boilers, the stationary internal combustion engines used in pipelines and gas-plants, domestic and commercial sources, and finally, non-combustion sources. The contribution of the last sector has been estimated to represent only 2% on a nation-wide basis (up to 5% without controls), between now and the year 2000. Thus, the stationary NO_x emission problem has been clearly identified as resulting from the combustion of fossil fuels in various applications, while non-combustion sources, such as plants manufacturing or using nitric acid are relevant only as "local nuisance", health and aesthetic problems.

Combustion modification techniques have been found to yield potentially effective solutions to the problem of NO_x control. Actual data on the effectiveness of combustion modifications are based on emissions from only a few gas or oil fired installations for which inexpensive methods have been applied. Further R&D work is required to establish the overall applicability, validity and optimization of these techniques. Also, since virtually no test data are available for coal-fired equipment, the applicability of combustion modification techniques for NO_x control in this use, without affecting overall operability is hypothetical at present. A major R&D effort is deemed necessary to define the scope of combustion modification techniques applicable to coal firing.

As part of the study a "first-generation" mathematical model has been formulated and used to predict NO_x formation rates from natural gas fired equipment. Results obtained using this model are in directional agreement with known trends affecting NO_x formation. Its basic features may be expanded to make it a useful guide for the design of low NO_x emission combustion equipment.

Combustion flue gas treatment methods are faced with major development and economic limitations. Short of an unlikely technological breakthrough, direct catalytic decomposition of NO_x does not appear to be feasible. However, certain scrubbing techniques which may recover both SO_x and NO_x may be potentially attractive, particularly for the control of emissions from large coal-fired installations, for which combustion modification techniques may not be applicable.

Other industrial modifications such as fuel substitution, fuel conversion, remote location of power plants or other large volume emission sources may have beneficial effects for NO_x control. However, in this area, major impact is expected from the increasing installation of nuclear-electric generation capacity. No emissions of NO_x are associated with nuclear generation.

The assessment of cost-effectiveness provides the basis for the development of alternate 5-year R&D plans on stationary NO_x emission control. The required program items have been ranked according to priority based on potential accomplishments in NO_x control at several alternate R&D funding levels. Rough R&D costs have been estimated to provide guidance for the implementation of a flexible, nation-wide program for stationary NO_x emission control.

Successful completion of the research, development and demonstration plans outlined could have a major effect on reducing NO_x emissions from stationary sources. For example, 1980 emissions might be cut back to pre-1950 levels.

The overall R&D program recommendations show good prospects for the control of NO_x emissions for all major emission sectors - power plants by combustion modification and/or flue gas treatment; industrial boilers and gas engines by combustion modifications.

1.1 CHARACTERIZATION OF THE NO_x EMISSION PROBLEM FOR STATIONARY SOURCES

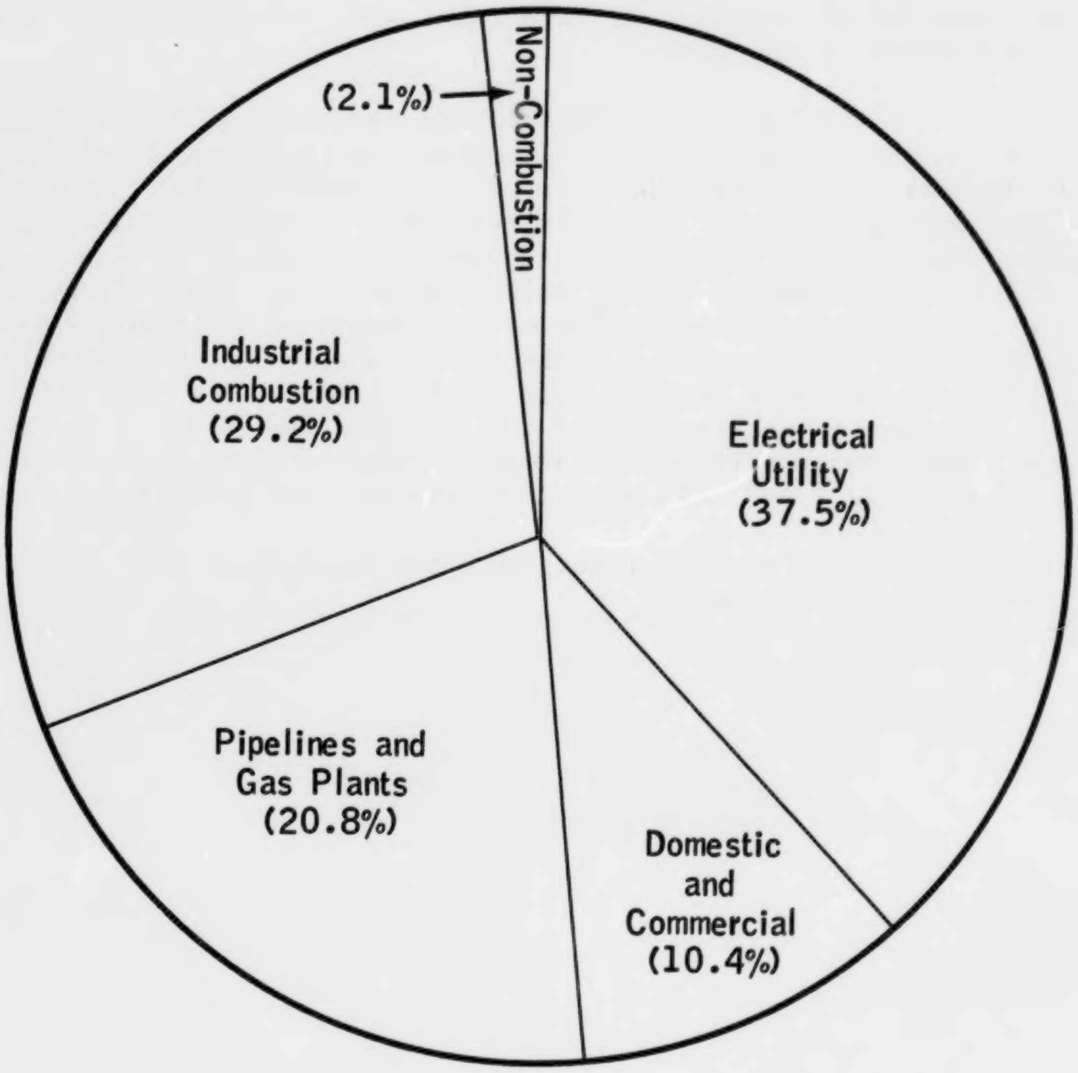
The NO_x emission problem for stationary sources has been characterized by emission source sector and fuel type, for the period between 1950 and the present, with projections and forecasts to the year 2000. Changes in the magnitude of the problem due to varying economic, technological, and socio-political trends have been taken into account in this problem definition phase of the study.

Oxides of nitrogen are formed in all air-burning fossil fuel combustion processes. Some NO_x is also emitted by non-combustion sources, primarily chemical plants manufacturing or using nitric acid. To estimate the NO_x emissions on an historical basis from 1950 to date, and project the emissions for the future, a variety of information sources have been utilized. To obtain information on NO_x emissions and fuel usage by type and consumer sector, a detailed review of the pertinent literature was conducted, backed up by a survey of field contacts and a steam-electric plant survey conducted as a part of this study. New survey data were also obtained on relevant operations in the oil and gas industry. Other major industrial, commercial and household sectors were surveyed using a combination of statistical data, published information, and field survey contacts.

NO_x emissions from stationary sources in the U.S. for 1968 are shown by categories in Figure 1-1.

Figure 1-1

TOTAL NO_x EMITTED IN THE U.S. FROM STATIONARY INSTALLATIONS, 1968



NO_x, Estimated Tons*, 1968	Type of Installation
3,600,000	Electrical Utility
2,800,000	Industrial Combustion
2,000,000	Pipelines and Gas Plants
1,000,000	Domestic and Commercial
200,000	Non-Combustion
9,600,000	U.S. TOTAL

*Calculated as NO_2.

The following ranking of stationary NO_x emission sources has been established:

1. Electric power plants.
2. Industrial combustion sources.
3. Stationary internal combustion engines used in pipelines and gas plants.
4. Domestic and commercial combustion equipment.
5. Non-combustion sources.

The very important role of coal used as a fossil fuel in electric power generation makes this fuel a major factor in stationary NO_x emissions.

Estimated NO_x emissions assuming the continuation of current practices (minimum level of control) are shown in Figure 1-2. NO_x emissions from mobile sources are also shown in Figure 1-2 for comparison. It is evident that stationary sources contribute over one-half of the total NO_x emissions, nation-wide. This situation is expected to continue into the future, particularly because of legislative emphasis on the control of motor vehicle emissions.

As a base point, stationary NO_x emissions on a completely uncontrolled basis have been estimated for several representative years between 1950 and 2000. The year 1980 is particularly significant. It is close enough to the present for making reasonably accurate projections, which in turn, can provide the basis for the formulation of realistic R&D plans on stationary NO_x control. The contribution of the principal individual source sectors to stationary NO_x emissions (on an uncontrolled basis) is presented for 1980 in Table 1-1.

Figure 1-2

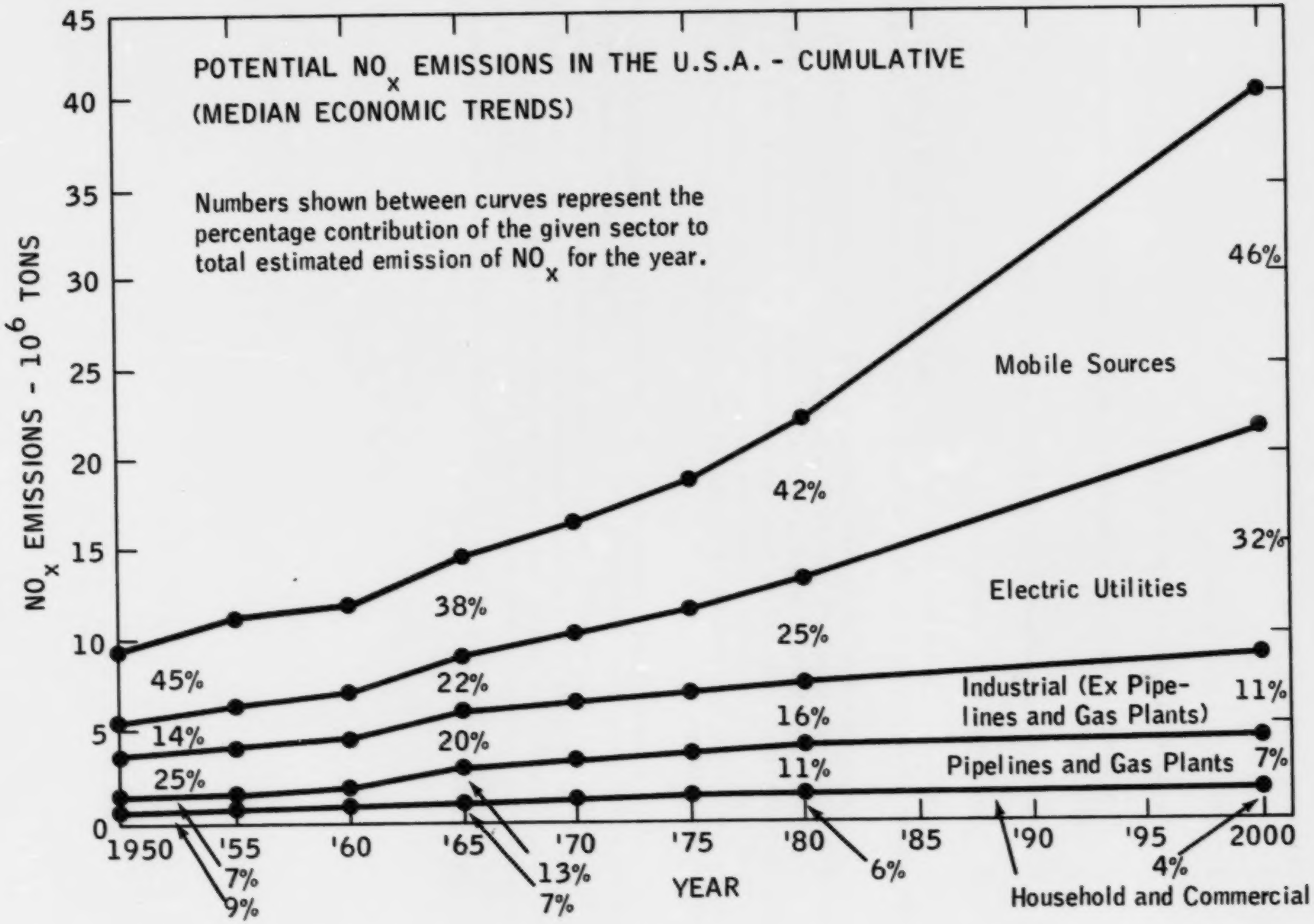

POTENTIAL NO_x EMISSIONS IN THE U.S.A. - CUMULATIVE
(MEDIAN ECONOMIC TRENDS)
Numbers shown between curves represent the percentage contribution of the given sector to total estimated emission of NO_x for the year.
NO_x EMISSIONS - 10^6 TONS
0
5
10
15
20
25
30
35
40
45
1950
'55
'60
'65
'70
'75
'80
'85
'90
'95
2000
YEAR
Mobile Sources
Electric Utilities
Industrial (Ex Pipelines and Gas Plants)
Pipelines and Gas Plants
Household and Commercial
45%
38%
42%
46%
14%
22%
25%
32%
25%
20%
16%
11%
7%
13%
11%
7%
9%
7%
6%
4%

Table 1-1

Potential Emissions From Major Stationary Sources - Year 1980

Major Source		Potential Emissions (Uncontrolled) 10^6 Tons	% of Total
1. Power Plants:		8.8	55
Coal	5.6		
Gas	2.3		
Oil	0.9		
2. Pipeline Engines		1.8	11
3. Industrial Boilers		1.5	9
4. Gas Plant Piston Engines:		0.6	4
• Less than 300 HP	0.02		
• 300-1800 HP	0.33		
• 1800 + HP	0.21		
5. Nitric Acid Plants:		0.3	2
Old	0.16		
New	0.13		
6. Refinery Sources:		0.3	2
Furnaces	0.20		
I.C. Engines	0.09		
		13.3	83
7. All Other Sources:		2.8	17
Household & Commercial	1.2		
Other Industrial	1.5		
Total Stationary		16.1	100

As seen from Table 1-1, the projected ranking of stationary NO_x emission sources for 1980 is in the same order as that found for 1968 in Figure 1-1. Consequently, this overall ranking of emission sources has been used in this study to guide the assessment of control technology for NO_x emission control.

1.2 CONTROL OF NO_x EMISSIONS BY COMBUSTION MODIFICATIONS

Oxides of nitrogen are produced in all fossil fuel combustion processes using air as the oxidant. At flame temperatures, the combination of atmospheric oxygen and nitrogen results in the formation of nitric oxide (NO). Although NO is thermodynamically unstable at lower temperatures, its decomposition is kinetically limited, since the activation energy for NO decomposition is on the order of 90 kcal/mole. Therefore, its concentration remains "frozen" as heat is removed from the combustion gases.

For most stationary combustion processes, the residence time available is too short for the oxidation of nitric oxide to nitrogen dioxide, the thermodynamically favored specie at lower temperatures. As a result, no more than 5-10% of this reaction takes place. Thus, although NO_x emissions are usually expressed as "equivalent NO_2," the combustion gases are predominantly in the form of NO.

In addition to fixation of N_2 with O_2, some of the nitrogen in the fuel is also converted into NO_x in combustion processes, based on experimental evidence. The role of fuel nitrogen appears to vary from being dominant at low temperatures to being negligible at high temperatures, i.e., near equilibrium conditions.

The atmospheric fixation of nitrogen with oxygen is represented by the overall reaction:

$$N_2 + O_2 \rightleftharpoons 2NO \qquad (1\text{-}1)$$

for which the thermodynamic equilibrium is given by

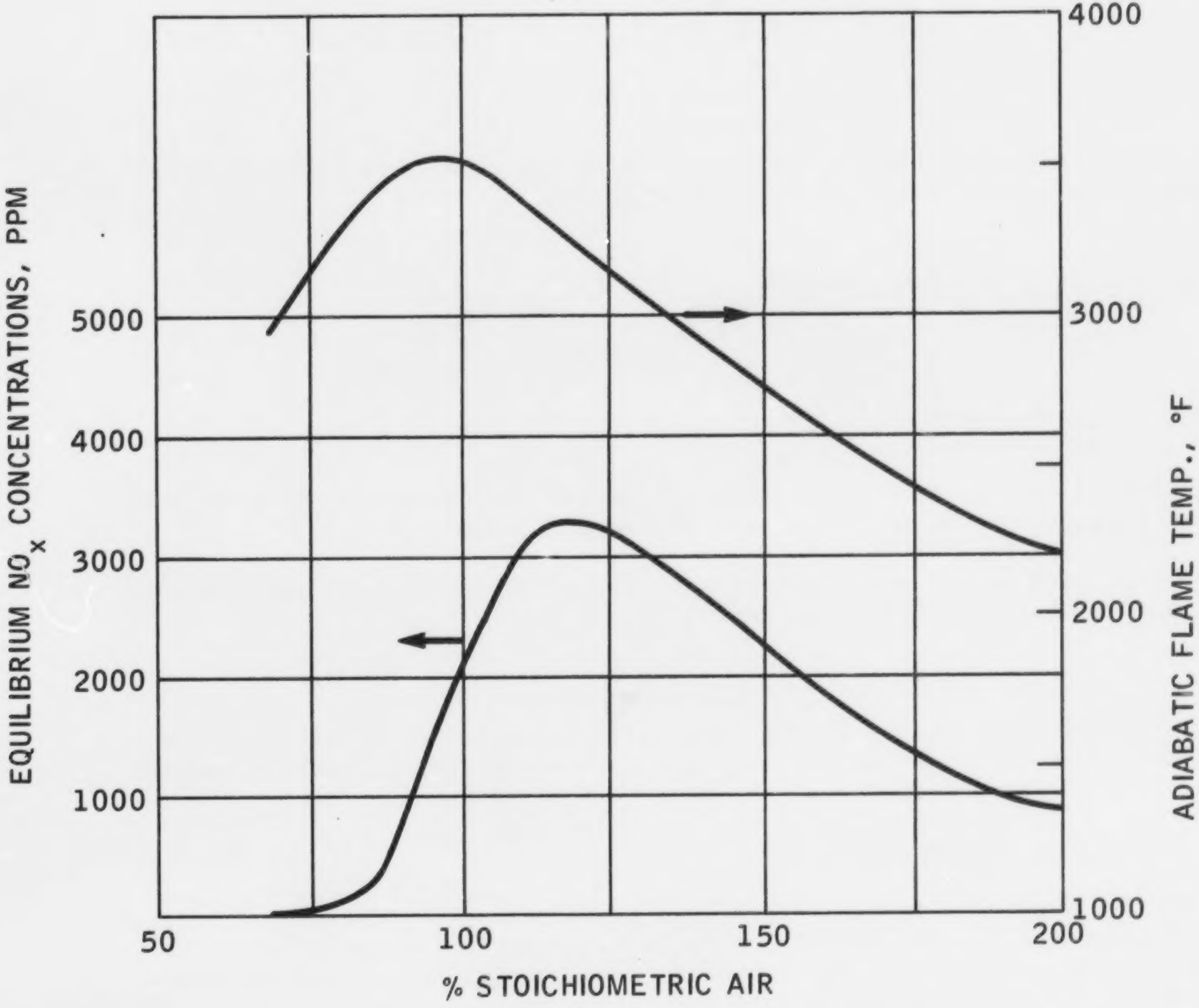
$$K_{eq} = \frac{(NO)^2}{(N_2)(O_2)} = 21.9e^{-43,400/RT} \qquad (1\text{-}2)$$

In Equation (1-2) (NO), (N_2), and (O_2) are in mole fractions or consistent concentration units; R is the gas constant (1.988 cal/g mole/°K); and T is the absolute temperature in °K.

Equilibrium NO_x concentrations and corresponding adiabatic flame temperatures are shown in Figure 1-3 for methane combustion at atmospheric pressure as a function of the % stoichiometric air supplied. The peak

Figure 1-3

NO_x EQUILIBRIUM IN METHANE-AIR FLAMES



equilibrium concentration of NO_x occurs at about 15% excess air, while the maximum adiabatic flame temperature is reached at slightly substoichiometric air/fuel ratios. At flame temperatures, the amount of NO_2 is negligible with respect to NO.

The rate of NO formation (as well as its rate of decomposition) is very highly temperature-dependent. The mechanism of NO formation has been shown to occur via the following chain reaction:

$$O_2 + M \rightleftharpoons 2O + M \qquad (1\text{-}3)$$

$$O + N_2 \rightleftharpoons NO + N \qquad (1\text{-}4)$$

$$N + O_2 \rightleftharpoons NO + O \qquad (1\text{-}5)$$

A steady state treatment of Equations (1-3) through (1-5) yields the following equation for the net rate of NO formation:

$$\frac{d(NO)}{dt} = 9 \times 10^{14} e^{-135{,}000/RT} (N_2)(O_2)^{1/2} - 4.1 \times 10^{13} e^{-91{,}600/RT} (NO)^2 (O_2)^{-1/2} \qquad (1\text{-}6)$$

g. moles/cc/sec

Equation (1-6) assumes equilibrium for oxygen atom formation from oxygen molecules, and is valid only in the presence of excess air.

The major known factors influencing NO_x emissions from combustion processes are summarized below:

(A) Excess Air

Low excess air firing results in reducing NO_x emissions. The lowest level of excess air permissible without operating problems depends on the combustion process and the type of fuel used.

(B) Heat Release and Mixing

High heat release rates lead to increased NO_x emissions, because of the extreme sensitivity of NO_x formation equilibrium and kinetics to peak temperatures. High heat removal (or quenching rates) are desirable, on the other hand, for stationary combustion processes, as they limit the exposure of the combustion gases to the highest temperatures. Thus, kinetic limitations are imposed on the amount of NO_x formed in the process.

(C) Mass Transport and Mixing

The distribution of fuel and air, and their mixing with combustion gases can affect NO_x emissions. Deliberate "imbalances" created to consume most of the fuel under fuel rich conditions may result in reducing NO_x emissions. Similarly, internal recirculation or backmixing of combustion gases dilutes the primary flame zone, reducing its temperature, which is desirable for limiting NO_x formation rates.

(D) Fuel Type and Composition

Fuel type affects NO_x formation both through the theoretical flame temperatures attainable (coal > oil > gas), and through the rate of radiative heat transfer (coal > oil > gas). These coupled factors may balance each other, but in general, for small to intermediate combustion installations it is a good "rule-of-thumb" to rank NO_x emission forming tendencies in the order: coal > oil > gas. For large installations, limited evidence indicates that this order may be reversed, presumably due to the shift in heat release/heat removal ratios.

Combustion modification techniques for NO_x control consist of modifying operating or design features. In some cases, both operating and design features may be modified to obtain optimum NO_x control. The most important modification techniques are listed below.

1.2.1 Modification of Operating Conditions

- Low excess air firing

  The effectiveness of low excess air firing is well documented for gas and oil combustion. No test data are available for commercial coal firing equipment. In coal firing, serious imbalances in fuel/air distribution may result, and problems of unburned fuel or carbon monoxide emissions may limit the utility of this approach.

- Two-stage combustion

  By supplying substoichiometric quantities of primary air to the burners in oil or gas-fired combustion, substantial reductions in NO_x emissions may be achieved. Complete burn-out of the fuel is accomplished by injecting secondary air at lower temperatures, where NO formation is limited by kinetics. This technique is best used in conjunction with low excess air firing. Reductions as high as 90% have been achieved by this combination, in large gas-fired power plants. Only laboratory data are available on the application of this technique to coal firing, where problems similar to those encountered with low excess air firing are expected.

- Flue gas recirculation

  This technique lowers the peak flame temperatures by diluting the primary flame zone with recirculated combustion flue gases. The oxygen concentration is also lowered, which favors reductions in NO_x emissions.

- Steam or water injection

  Injection of low temperature water or steam is similar in concept to flue gas recirculation--thermal dilution of the flame can be achieved, resulting in reduced NO_x emissions. This technique appears to have limited utility for NO_x control for furnaces because of operating debits. However, in laboratory studies in internal combustion engines it has been shown to be very effective for the control of NO_x emissions, apparently without affecting the cycle efficiency.

- Combination of combustion modification techniques

  The combination of combustion modification techniques appears to be the best approach to NO_x control. This has been demonstrated both in full scale and laboratory equipment. Further research is required to validate broadly the limited data available, to define potential problems, and ultimately to optimize techniques.

1.2.2 Modification of Design Features

- Burner configuration, location and spacing

  Variations in NO_x emission levels have been observed with different types of burners. For example, the highly turbulent operating features of cyclone burners result in high level NO_x emissions in coal-fired power plants.

  More importantly, spacing the burners in such a manner that radiative heat transfer is increased can reduce NO_x emissions, in accord with the theoretical considerations discussed earlier. This is especially important for large power plant furnace operations.

- Tangential firing

  In tangential firing, the furnace itself is used as the burner, resulting in lower peak flame temperatures, and corresponding reductions in NO_x emissions. As much as 50-60% reductions in NO_x levels have been reported, compared with conventional methods of firing. Further studies are required for optimizing this approach in combination with other combustion modification techniques.

- Fluid bed combustion

  This technique is a useful design concept now under development, which offers very high heat transfer rates, and hence low average combustor bed temperatures. In spite of this, the oxidation of fuel nitrogen presents a problem, but the fluid bed technique offers the potential advantage of controlling both SO_x and NO_x by the addition of limestone or similar material directly into the combustion zone.

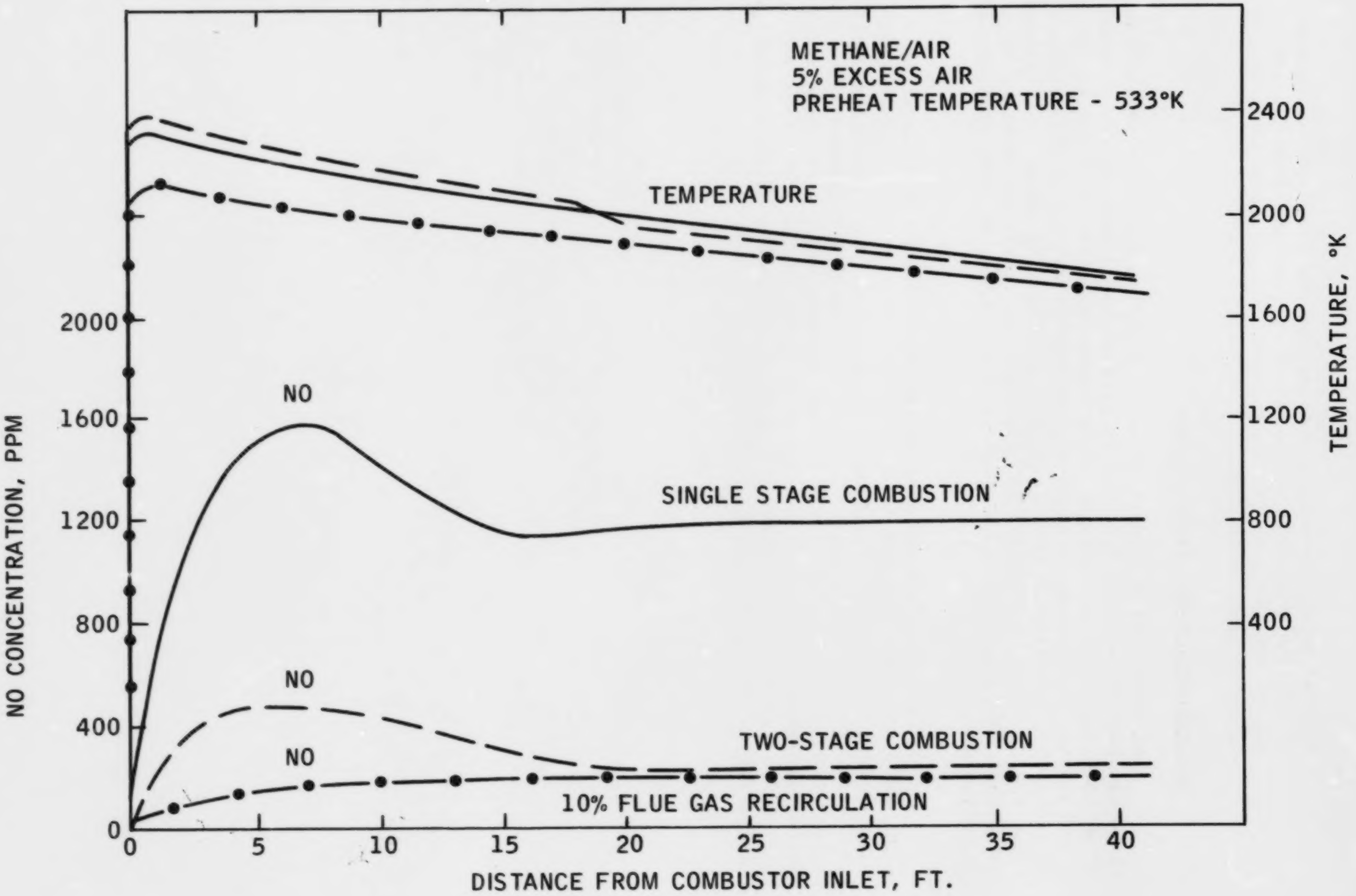
1.2.3 Mathematical Model Predictions

An idealized mathematical model based on the theories outlined above has been formulated and used to predict the formation and decomposition of NO in natural gas combustion. This "first generation" model is capable of predicting directional effects of varying operating and designing parameters on NO_x emissions. In line with experience, it shows lowering peak flame temperatures and excess air level both to result in lowering NO_x emissions. For high quenching rates in the furnace, it also predicts lower NO_x emissions.

Typical predictions made by the model on the effects of two-stage combustion and flue gas recirculation, compared with conventional "single-stage" combustion are shown in Figure 1-4. This idealized model lends itself to extending its scope to provide more realistic information. Additional factors to be incorporated include kinetic data, heat, mass and momentum transport effects, and extension to other fossil fuels (oil and coal). This will be required to achieve the goal of making the model a useful guide for the design of low NO_x emitting combustion equipment.

Figure 1-4

TYPICAL NO-TEMPERATURE PROFILES PREDICTED BY THE MATHEMATICAL MODEL: EFFECTS OF TWO-STAGE COMBUSTION AND FLUE GAS RECIRCULATION



1.2.4 Combustion Modification Control Costs

The potential degree of NO_x emission control is difficult to predict, because of the large variety of emission sources having different design and operating characteristics. The estimated effectiveness of combustion modification techniques used in this study are illustrated in Table 1-2. These estimates are based on actual information, where available; otherwise, conservative estimates of the degree of NO_x reduction have been made. It is clear again that the combination of combustion modification techniques may result in more effective control of NO_x emissions. These control methods are relatively simple, do not require large capital investments, and the operating costs are low. In fact, in the case of low excess air firing, there are even estimated to be operating credits. Typical cost estimates presented in Table 1-3 show the application of various combustion modification techniques for NO_x control in 1000 MW utility boilers. The annual costs presented in this table include capital charges, operating costs, operating credits due to fuel savings, and reduced maintenance costs where applicable. The estimates shown in Table 1-3 indicate the potential economic attractiveness of some of these techniques.

A systematic study of the applicability and limitations of these techniques is required before their general usefulness can be established. Such a study is recommended as a prime component of the five-year R&D program plan.

Combustion modification techniques also show an attractive potential for NO_x emission control from other major fossil fuel combustion sources--industrial boilers and internal combustion engines.

For industrial boilers, the most cost-effective combustion modification method appears to be low-excess air firing. Under favorable conditions, it has been estimated that this technique may result in net savings due to fuel economies. Flue gas recirculation may also be feasible. The application of two-stage combustion techniques for this equipment category appears to be restricted, because of the large number of single-burner installations. However, new units may be designed to take advantage of this technique.

The control of NO_x emissions from stationary internal combustion engines (primarily gas engines) appears to be feasible via water injection, but this approach must be validated by R&D work. The trend toward gas turbine drivers for compressors may lessen the importance of this sector.

Table 1-2

Public Utility Boilers: Estimated % NO_x Reduction By Combustion Modifications

Boiler Size	LEA(1)	Two-Stage	LEA + Two-Stage	FGR(2)	LEA + FGR	Water Injection
1000 MW						
Gas	33	50	90	33	80	10
Oil	33	40	73	33	70	10
Coal	25	35	60	33	55	10
750 MW						
Gas	33	50	85	33	80	10
Oil	33	40	73	33	70	10
Coal	25	35	60	33	55	10
500 MW						
Gas	33	50	70	33	70	10
Oil	33	40	65	33	65	10
Coal	25	35	55	33	55	10
250 MW						
Gas	33	45	60	30	60	10
Oil	30	35	55	30	55	10
Coal	25	30	50	30	50	10
120 MW						
Gas	33	40	53	30	53	10
Oil	30	30	45	30	45	10
Coal	25	25	40	30	40	10

(1) LEA: Low excess air firing.

(2) FGR: Flue gas recirculation for NO_x control.

Table 1-3

Public Utility Boilers

Combustion Modification Control Costs

Boiler Size 1000 MW Fuel Gas Load Factor 6120 Hrs/Hr

	Fixed Costs			Operating Costs		
Control Method	Start-Up Costs $1000	Capital Eq Costs $1000	Capital Charges $1000	Maint., Suppl. and Overhead $1000	Other Oper. Costs $1000	Total Cost Per Year $1000
Low Excess Air		120	17	21	(133)*	(95)
2-Stage Combustion		0	0	0	0	0
Low Excess Air + 2 Stage Combustion		120	17	21	(133)	(95)
Flue Gas Recirculation		600	84	52	66	202
Low Excess Air + Flue Gas Recirculation		720	101	73	(67)	107
Water Injection		23	3	2	139	144

---

*Figures in parenthesis indicate operating savings.

1.3 CONTROL OF NO_x EMISSIONS BY COMBUSTION FLUE GAS TREATMENT

While combustion modification techniques are aimed at preventing NO_x formation, removal of nitrogen oxides from flue gases provides a potential alternate method for controlling combustion-related emissions. Although the concentrations of nitrogen oxides in flue gases are low, the volumes of gas emitted by large installations are so great that significant amounts of these contaminants are released into the atmosphere on an individual plant basis. (see Table 1-4).

Table 1-4

Quantities of Gases and Nitrogen Oxides Emitted by Typical Power Plants

Power Plant	Volume of Gases Released, 10^6 SCFH	Lbs/Hr NO_x Released (Calculated as NO_2)
750 MW Gas Fired	73	9,516
750 MW Coal Fired	83	7,325
250 MW Gas Fired	29	1,237
250 MW Coal Fired	32	2,478

The processing of such large volumes of gas for NO_x emission control presents formidable engineering problems in gas contacting, equipment size, pressure drop, temperature control, etc. Furthermore, other flue gas species such as moisture, CO_2, SO_2 and O_2 often interfere with removal processes using sorption, scrubbing and catalytic conversion techniques. This is particularly true for the removal of low concentrations of NO_x.

Combustion flue gas treatment processes have been evaluated in the following general categories:

- Catalytic decomposition of NO_x.
- Catalytic reduction of NO_x
  - Selective reduction under net oxidizing conditions
  - Non-selective reduction under net reducing conditions.
- Adsorption processes.
- Absorption processes.
- Physical separation.

The assessment of existing and potential NO_x control technology has resulted in the following major conclusions:

A. Aqueous scrubbing systems using aqueous alkaline solutions or concentrated sulfuric acid appear to offer the best potential for the control of both sulfur and nitrogen oxide emissions from flue gases. To be effective, equimolar concentrations of NO and NO_2 (equivalent to N_2O_3) are needed in the flue gas. Known homogeneous or catalytic oxidation techniques are too slow or costly for achieving such equimolar concentrations. The recycle of NO_2 into the flue gas appears to offer the best possibility. This recycle of NO_2 may be accomplished by oxidizing the concentrated NO stream produced by thermal, catalytic or chemical regeneration of the spent absorbent.

B. Selective reduction of NO_x with ammonia, hydrogen sulfide, or hydrogen is a less likely possibility. Such approaches have been demonstrated under laboratory conditions. The use of ammonia or hydrogen sulfide as selective reductants would permit the control of SO_2 emissions also. Research is needed to develop catalytic processes suitable for use at flue gas concentrations and acceptable from the standpoint of catalyst cost, life, and activity.

C. Common adsorbents such as silica gel, alumina, molecular sieves, char and ion exchange resins all show some capacity for oxidizing NO to NO_2 and then adsorbing the nitrogen dioxide. However, the capacities of these adsorbents are quite low at typical NO flue gas concentrations. Among solid sorbents, certain metal oxides, particularly manganese and alkalized ferric oxides show technical potential, especially in conjunction with a regenerative system with recycle of NO_2 into the flue gas. However, sorbent attrition under the severe conditions required for flue gas treatment is a major technological stumbling block for developing such processes.

D. To date, no flue gas treatment process has been directly applied to NO_x emission control in power plants.

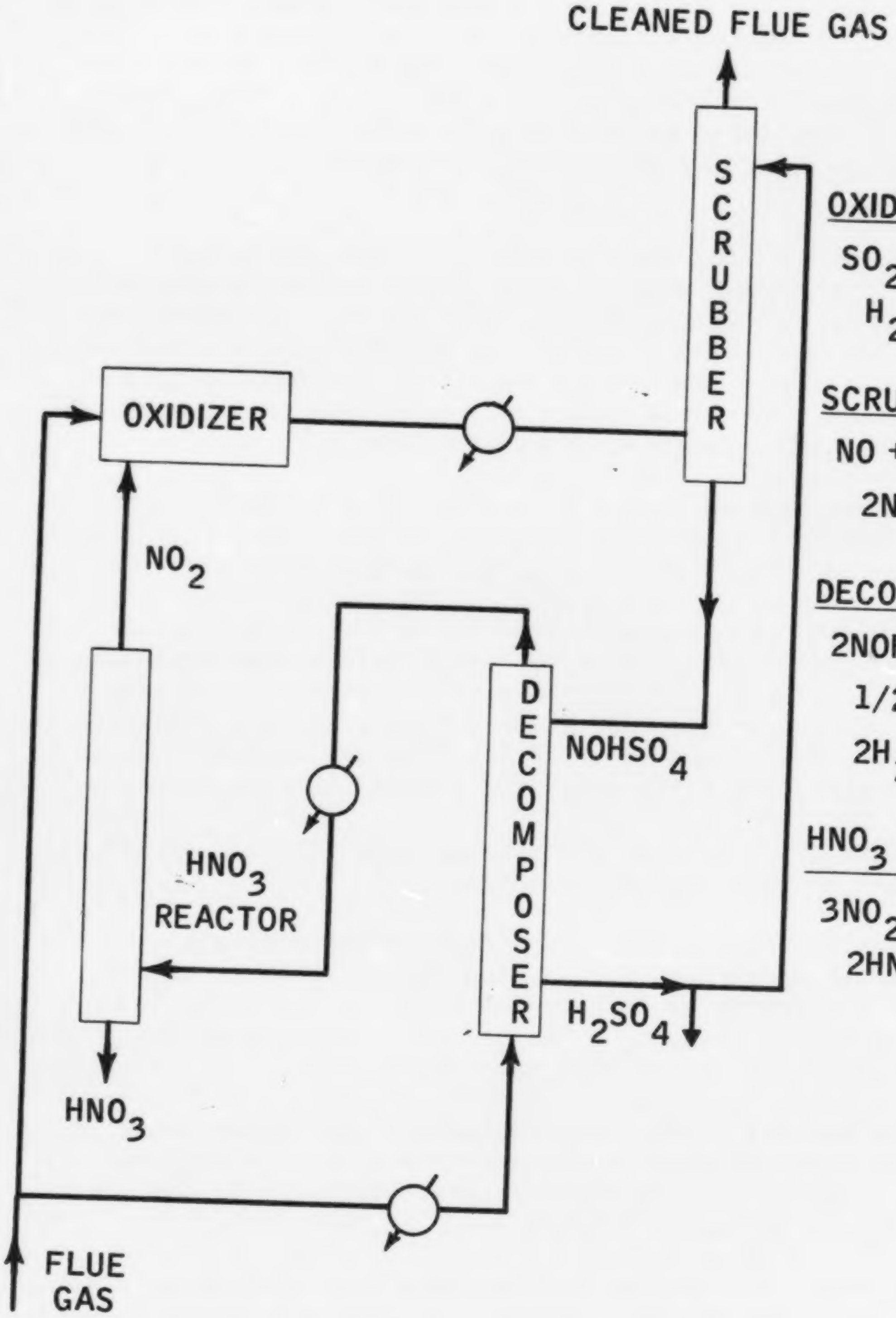
E. No catalyst has been found which is effective for a simple, low investment NO decomposition process, and the probability of uncovering such a catalyst by further R&D work appears to be low. However, in fluid bed combustion the use of certain alkali or alkaline additives appears to show some promise.

F. Success in the removal of NO_x from combustion flue gases based on differences in physical characteristics such as molecular size, condensation temperature, or magnetic susceptibility of the components appears to be highly remote.

As discussed above, scrubbing of flue gases with concentrated sulfuric acid, in conjunction with NO_2 recycle into the flue gas, shows potential for the control of both SO_x and NO_x emissions. In this connection, Tyco Laboratories (Contract No. PH 86-69-75) are studying possible modifications of the Lead Chamber Acid Process. The Tyco process is shown schematically in Figure 1-5. Since NO_2 is required here for the oxidation of SO_2 to SO_3, very

Figure 1-5

TYCO'S MODIFIED SULFURIC ACID SCRUBBING PROCESS


CLEANED FLUE GAS
SCRUBBER
OXIDIZER
NO_2
HNO_3 REACTOR
DECOMPOSER
$NOHSO_4$
H_2SO_4
HNO_3
FLUE GAS

OXIDIZER

$SO_2 + NO_2 + H_2O \rightarrow$
$H_2SO_4 + NO$

SCRUBBER

$NO + NO_2 + H_2SO_4 \rightarrow$
$2NOHSO_4 + H_2O$

DECOMPOSER

$2NOHSO_4 + H_2O +$
$1/2\ O_2 \rightarrow 2NO_2$
$2H_2SO_4$

HNO_3 REACTOR

$3NO_2 + H_2O \rightarrow$
$2HNO_3 + NO$

stringent requirements are placed on the scrubber efficiency in order to supply the necessary NO_2. This factor is illustrated by the data in Table 1-5. In the extreme case of only 90% scrubber efficiency, 77% of the original NO in the flue gas would not be absorbed. Consequently, costs in the sulfuric acid absorption process are highly sensitive to scrubber efficiency. This effect is illustrated by the range of costs varying from about \$20/ton NO_x removal at 98% scrubber efficiency, to about \$60 to \$120/ton NO_x removal at 92% scrubber efficiency, for 1000 MW coal or oil-fired power plants, respectively.

Table 1-5

Effect of Flue Gas SO_2 and NO Concentration on Recycle Requirements of the Tyco Processes

SO_2 Content of Flue Gas, ppm	NO Content of Flue Gas, ppm			
	500	700	1000	1500
	NO_2 Recycle Requirements			
2000	4500	4700	5000	5500
3000	6500	6700	7000	7500

Among potential alkaline scrubbing systems, those utilizing limewater,and particularly magnesium hydroxide solutions show the best promise. Recycle of NO_2 into the flue gas is required as in the case of the modified Lead Chamber Acid Process, to make NO absorption possible by supplying equimolar proportions of NO_2. Potential limewater and magnesium hydroxide scrubbing processes are illustrated schematically in Figures 1-6 and 1-7, respectively. For 1000 MW power plants, the estimated costs of these processes are summarized in Table 1-6. Operating costs are strongly dependent on power plant size and fuel type. For the 1000 MW coal-fired plant shown in Table 1-6, the $Mg(OH)_2$ scrubbing system is estimated to yield a net profit.

Figure 1-6

POTENTIAL LIMEWATER SCRUBBING SYSTEM

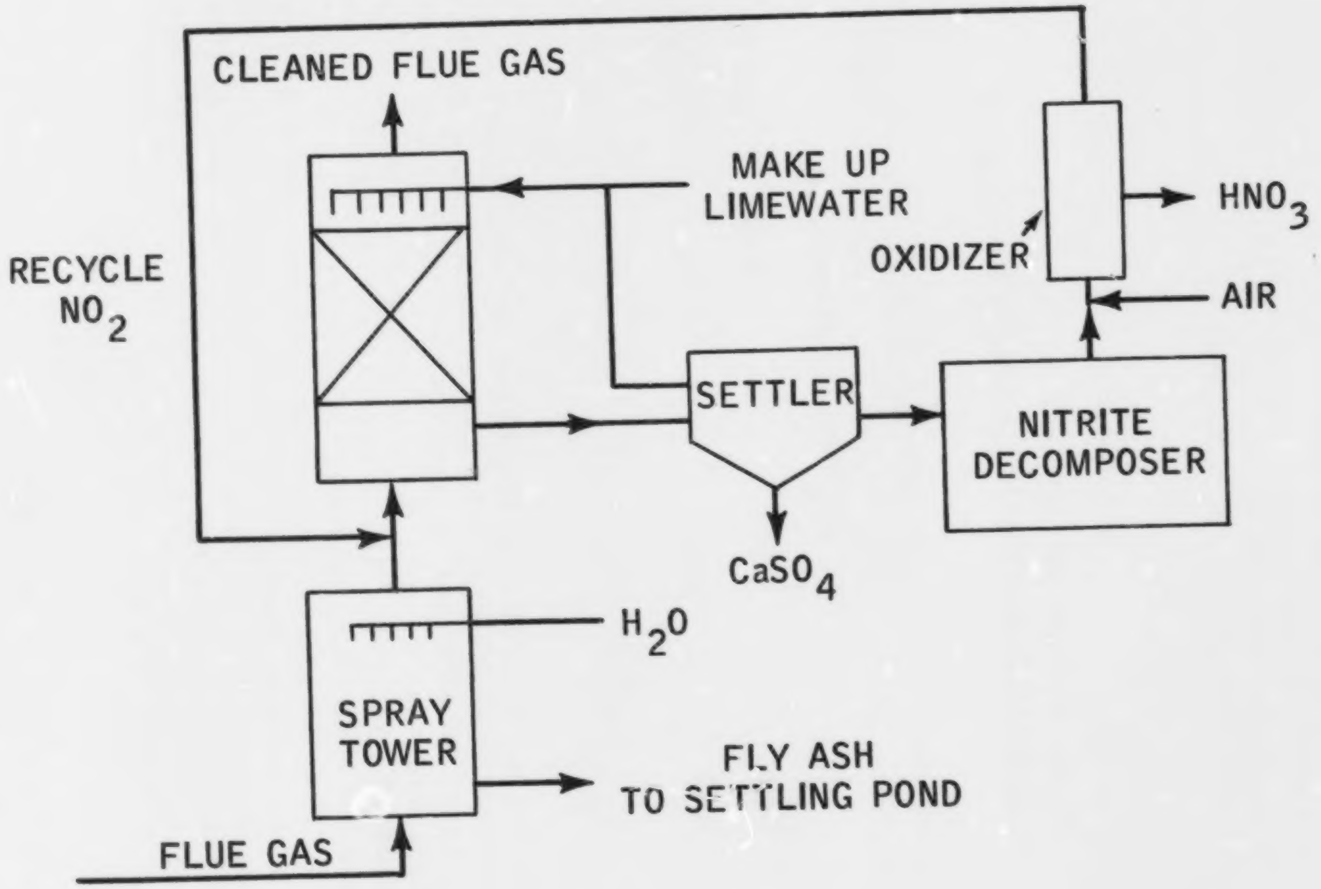

CLEANED FLUE GAS
MAKE UP LIMEWATER
RECYCLE NO_2
OXIDIZER
HNO_3
AIR
SETTLER
NITRITE DECOMPOSER
$CaSO_4$
H_2O
SPRAY TOWER
FLY ASH TO SETTLING POND
FLUE GAS

Figure 1-7

POTENTIAL $Mg(OH)_2$ SCRUBBING SYSTEM

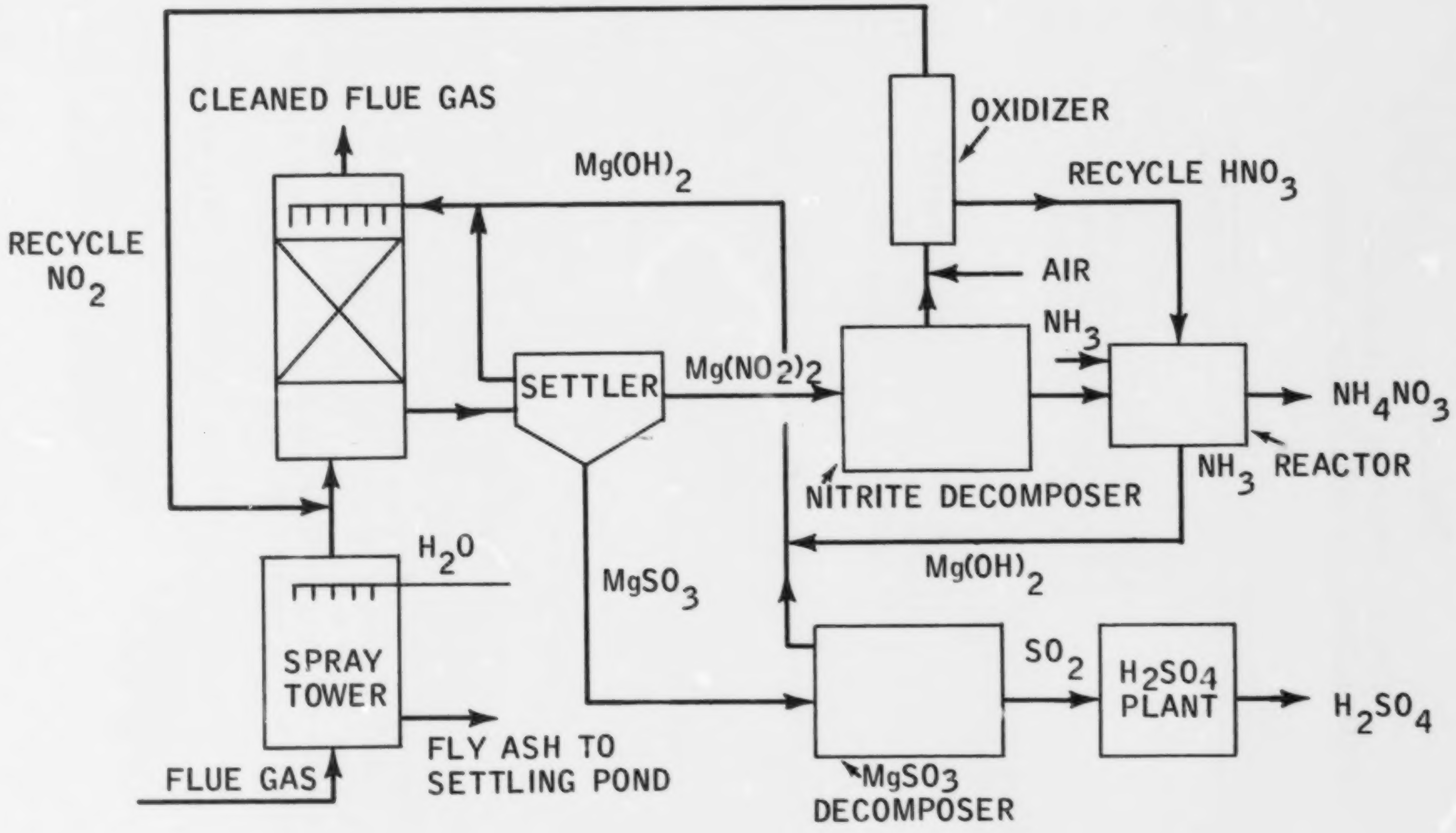

RECYCLE NO_2
CLEANED FLUE GAS
$Mg(OH)_2$
OXIDIZER
RECYCLE HNO_3
AIR
NH_3
SETTLER
$Mg(NO_2)_2$
NH_4NO_3
NH_3
REACTOR
NITRITE DECOMPOSER
H_2O
$Mg(OH)_2$
$MgSO_3$
SPRAY TOWER
SO_2
H_2SO_4 PLANT
H_2SO_4
FLUE GAS
FLY ASH TO SETTLING POND
$MgSO_3$ DECOMPOSER

Table 1-6

Alkaline Scrubbing NO_x Emission Control Costs for 1000 MW Power Plants(1)

Process	Costs, $		$/Ton NO_x Removed
	Net Investment	Annual	
Limewater Scrubbing			
Coal	8,472,000	1,071,000	45
Oil	9,011,000	1,194,000	50
Gas	9,742,000	929,000	22
$Mg(OH)_2$ Scrubbing			
Coal	12,000,000	(122,000)(2)	(5)(2)
Oil	11,637,000	510,000	21
Gas	10,455,000	1,039,000	25

(1) Flue gas desulfurization credits assumed: $0.50/ton coal; $0.125/bbl oil.
(2) Profit.

Similar cost estimates have been made for all flue gas treatment processes considered in this study. These cost estimates may strongly vary with the size of the installation, fuel type, and product and operating credits assumed.

1.4 CONTROL OF NO_x EMISSIONS FROM NON-COMBUSTION SOURCES

Non-combustion sources play only a very small role in nation-wide NO_x emissions, from the systems standpoint. However, large individual emission sources are found among plants manufacturing or using nitric acid. This emission source category thus merits attention from the point of view of "local nuisance" health hazards and aesthetic values.

Major sources of such emissions and typical estimated control costs are summarized in Table 1-7.

Table 1-7

Control of NO_x Emissions From Typical Nitric Acid Operations

Chemical Process	Potential Control Processes	Control Cost $/Ton NO_x Removed
Nitric Acid Manufacture(1)	• Non-Selective Catalytic Reduction	
	- Decolorization and Power Recovery	Does not remove NO
	- Single-stage Abatement(2)	
	- Two-stage Abatement(3)	27
	• Selective Catalytic Reduction	34
	• Alkaline Scrubbing	
	• Adsorption Techniques	
Nitric Acid Uses		
1. Ammonium Nitrate Manufacture	• None needed	--
2. Organic Oxidation	• Absorption	Batch processes, no control costs estimated
	• Flame Incineration	
3. Organic Nitrations	• Caustic Scrubbing	
	• Flame Incineration	
	• Urea Addition	
4. Metals Treatment	• Urea Addition	50

(1) Basis: 300 T/D nitric acid plant; reduction of NO_x emissions from 3000 ppm to 300 ppm in tail gas.

(2) All fuel added at the same point.

(3) Fuel added in two stages; heat removal between stages to limit temperature rise.

Other minor non-combustion sources reviewed in this study include arc welding, electrostatic precipitators, and high level NO_x concentrations generated in agricultural silos. On a nationwide basis, these sources contribute an insignificant fraction of total stationary NO_x emissions, but they can represent localized spot hazard problems.

1.5 OTHER MEANS OF LIMITING EXPOSURE OF URBAN POPULATIONS TO NO_x EMISSIONS

The exposure of urban populations to NO_x emissions may be moderated by means other than engineering process controls. Several techniques in this category have been evaluated in this systems study.

The NO_x emission problem primarily affects urban-metropolitan areas. In such populated areas, man-made sources heavily over-shadow the natural background cycle of biological NO_x production and removal from the atmosphere. In this context even "remote location" may be regarded as, at best, a temporary control measure. However, regional considerations become of prime importance here: factors prevailing in different parts of the country, e.g., the Far-West, the Mid-West, or the Mid-Atlantic Eastern regions will be significantly different. By the same token, other means of reducing NO_x emissions, e.g., switching fuels or chemical raw materials are subject to similar regional considerations.

In this category the following principal approaches have been considered for potential control of urban population exposure to NO_x.

1.5.1 Fuel Switch

For most combustion applications, the magnitude of NO_x emissions is in the order coal > oil > gas. The composition of the fuel also has an effect, indicated by the lowering of NO_x emissions reported by California utility companies upon switching from a California fuel oil to a low-nitrogen, -sulfur, -metals containing paraffinic fuel oil.

In spite of potential reductions in NO_x emissions, wide-spread fuel substitutions have been judged unlikely because of potential adverse economic effects on the entire fuel supply structure.

1.5.2 Nuclear Power Generation

The substitution of nuclear generation for fossil fuel fired power generation is the most effective means of abating NO_x emissions. No NO_x emissions are associated with nuclear generation. This factor will have a major impact on NO_x emissions from power plants, considered in this report specifically for the Chicago region.

For the entire U.S., the substitution of nuclear generation for fossil fuel firing is estimated to reduce NO_x emissions by 3.6 million tons in 1980.

1.5.3 Remote Plant Location

With recent advances made in high voltage electrical transmission, mine-mouth generation at remote locations is a distinct possibility for preventing urban population exposure to NO_x emissions.

Similarly, plants manufacturing or using nitric acid may be relocated to remote locations. Nevertheless, economic considerations such as shipping costs of raw materials and products will determine the degree of use of such approaches.

1.5.4 Non-Conventional Power Generating Cycles

In place of the conventional Rankine cycle, future advanced thermal cycles may include multivapor cycles, exhaust fired cycles, supercharged boiler cycles, closed cycle gas turbine, and the magnetohydrodynamic (MHD) cycles.

Although none of these advanced cycles is expected to influence stationary NO_x emissions in a major way, their directional effects have been estimated. Among these advanced cycles, the successful development of MHD generation would give rise to very high concentrations of NO_x which might be turned into an advantage by successful flue gas treatment, resulting in the recovery of nitrogen oxides as nitric acid or ammonium nitrate.

1.6 COST-EFFECTIVENESS OF NO_x CONTROL

The prime objective for performing cost-effectiveness analyses in this study has been to provide a basis for guiding the development of the 5-year R&D plans on stationary NO_x control. Under no conditions should these cost-effectiveness analyses be treated as a guide for implementation of NO_x control technology, without carrying out the necessary R&D work.

Cost-effectiveness, in simple terms, is defined as the ratio of the annual control cost to the tons of NO_x (calculated as NO_2) removed. This basis in interconvertible with other bases, such as dollars per "ton of equivalent coal" or mils per KW hr for power plants.

The cost-effectiveness analyses become complex when applied to all major U.S. stationary NO_x emission sources. To put the regional nature of the NO_x problem into perspective, the cost-effectiveness analyses have been developed in the following steps, with increasing degrees of complexity:

- Single power plant boilers
- A complete power plant
- All power plants in two large urban-metropolitan regions:
  (1) Los Angeles County (oil and gas firing), and
  (2) The Chicago area (mainly coal, with some oil and gas)

- All U.S. fossil fuel burning steam-electric plants
- All major NO_x emission sources in the U.S.

The year 1980 was selected as the best year for these cost-effectiveness analyses. The advantage of selecting a single representative year instead of a time period such as 1970-2000 is that reasonably accurate forecasts are available, and the year chosen is sufficiently near to treat it as a real-time, realistic problem.

It must be recognized that the cost-effectiveness analyses are sensitive to both emission and cost estimates. However, it is felt that they provide a sufficiently accurate representation of potential accomplishments to offer guidance for planning the 5-year R&D program.

1.6.1 Regional Analyses

The regional cost-effectiveness analyses are illustrated here by the alternate profiles developed for Los Angeles County, in Figure 1-8. The solid line segments in this figure represent the following sequence of controls: substitution of paraffinic, low-nitrogen and -sulfur fuel oil for cracked residual oil; use of present version of the two-stage combustion process; application of low excess air firing (resulting in fuel economy); additional "modified" (minimal cost) two-stage combustion; flue gas recirculation; and water injection. The dashed lines in the figure are based on higher, more conservative cost estimates. Expenditures of such magnitude may be necessary for the application of low excess air and two-stage combustion, compared to the low-cost estimates based on actual operating data in a single California test. The degree of applicability of the "low cost" estimates remains to be determined in a systematic R&D project.

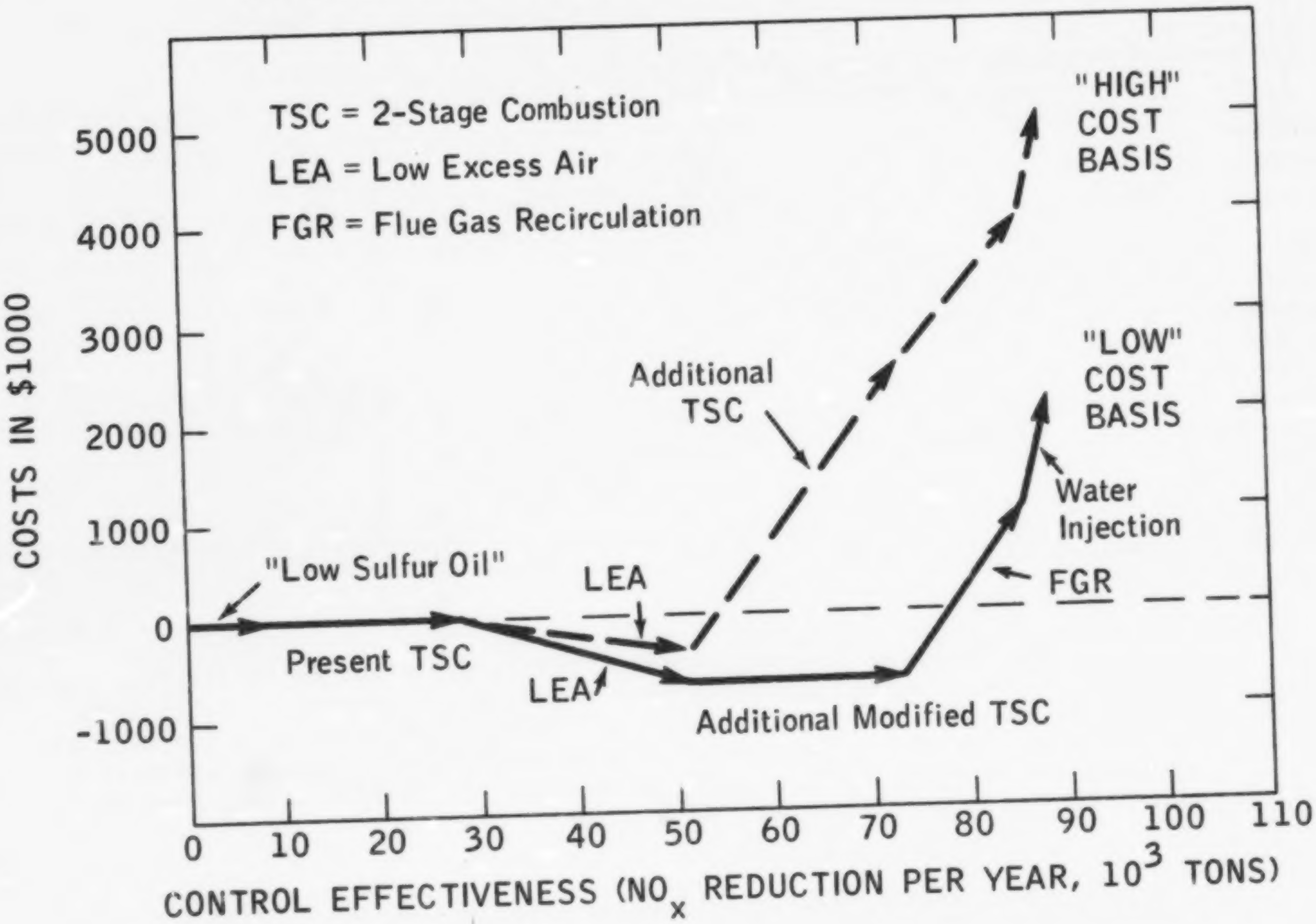
An interesting corollary of the analysis presented in Figure 1-8 is that it may be possible to accomplish a high degree of NO_x control at relatively modest costs, by combustion modification techniques. This provides further impetus for a detailed study of the potential applicability of these techniques.

1.6.2 Total U.S. Analyses

To estimate the effectiveness of NO_x control methods, "composite boilers" have been formulated as the basis for this study. This composite takes into account known variations in boiler design, method of firing and fuel type, on a weighted basis, and estimated boiler size distribution by categories for the year 1980. To arrive at realistic estimates of potential, uncontrolled NO_x emissions, the existing emission factor data for large boilers have been combined with pertinent information gathered in this study. Similarly, in other categories of equipment, e.g., for intermediate boilers, the projected 1980 population of boilers was divided into size categories, and the Los Angeles County emission factor curve data have been applied.

Figure 1-8

COST-EFFECTIVENESS PROFILES
LOS ANGELES COUNTY - YEAR 1980 PROJECTIONS



Using the above approaches, it was estimated that the potential, completely uncontrolled stationary NO_x emissions in the U.S. would be on the order of 16 million tons in 1980. (Continuation of current limited control practices would reduce this amount to about 13 million tons of NO_x in 1980.) To arrive at a given degree of reduction, a "minimum cost path" exists, which varies with the target reduction. This fact is illustrated in Table 1-8 by the estimated control cost for three levels of reductions in emissions, 8.9, 7.5 and 4.2 million tons of NO_x, respectively. The "negative" cost for the lowest reduction level results from the estimated savings realized from the application of low excess air firing for power plant and industrial boiler furnaces.

Table 1-8

Control Costs for Three U.S. NO_x Emission Reduction Targets

Emission Source	NO_x Emission Reduction Targets								
	8.9×10^6			7.5×10^6			4.2×10^6		
	NO_x Removed (10^3 Tons)	Ann. Cost ($\$10^6$)	$/Ton	NO_x Removed (10^3 Tons)	Ann. Cost ($\$10^6$)	$/Ton	NO_x Removed (10^3 Tons)	Ann. Cost ($\$10^6$)	$/Ton
Power Boilers	6,460	44.1	7	5,522	-6.6	-1	3,996	-26.1	-7
Pipelines	1,370	4.4	3	1,370	4.4	3	0	--	--
Gas Plants	405	2.6	6	405	2.6	6	0	--	--
Industrial Boilers	326	6.1	19	181	-0.5	-3	181	-0.5	-3
Nitric Acid	259	14.3	55	0	--	--	0	--	--
Refinery Engines	65	.7	11	62	0.5	8	25	0.03	1
Total	8,886	72.2	8	7,540	0.4	0.1	4,202	-26.5	-6

The "minimum cost NO_x control" points projected as of 1980 for all U.S. combustion sources and nitric acid plants are presented in Table 1-9. Although domestic sources are significant, no costs are included for the control of these sources. The cost of control of NO_x from domestic combustion has been estimated to be excessive, on the order of \$4000/ton NO_x removed, even under optimistic assumptions.

The complete cost-effectiveness profile developed in Table 1-9 to a removal of about 9 million tons of NO_x in 1980 is graphically shown in Figure 1-9. The "minimum cost" control points have been arrived at as discussed above, by determining the lowest control cost for removing the next increment of NO_x. Thus, incremental substitution cost means backing out already incorporated control costs and substituting the next lowest cost technique which is capable of the next increment of NO_x removal.

Table 1-9

Minimum Cost NO_x Control Points in 1980
United States Combustion and Nitric Acid Plant Sources

Emission Source	Fuel Burned	Control Method	Control Cost ($/Ton)	Incremental Substitution Cost* ($/Ton)	NO_x Removed/Yr (10^3 Tons) Indiv.	NO_x Removed/Yr (10^3 Tons) Cumul.	Cost Per Year ($1,000) Indiv.	Cost Per Year ($1,000) Cumul.
750 MW	Oil	LEA	-30.5		81	81	-2,486	-2,486
500 MW	Oil	LEA	-31.4		51	132	-1,584	-4,070
250 MW	Oil	LEA	-30.0		26	158	-792	-4,862
1000 MW	Oil	LEA + 2 St.	-13.6		197	355	-2,673	-7,535
1000 MW	Coal	LEA	-10.5		458	813	-4,819	-12,354
750 MW	Coal	LEA	-10.5		398	1,211	-4,189	-16,543
500 MW	Coal	LEA	-8.5		258	1,469	-2,187	-18,730
145 WT	Oil	LEA	-8.0		47	1,516	-376	-19,106
750 MW	Gas	LEA	-7.1		221	1,737	-1,564	-20,670
500 MW	Gas	LEA	-6.8		138	1,875	-945	-21,615
120 MW	Oil	LEA	-5.4		26	1,901	-142	-21,757
250 MW	Gas	LEA	-5.0		32	1,933	-160	-21,917
1000 MW	Coal	$Mg(OH)_2$	-5.1	-2.6	1,464	2,940	-7,437	-24,535
1000 MW	Gas	LEA + 2 St.	-2.0		954	3,894	-1,900	-26,435
188 WT	Coal	LEA	-1.2		57	3,951	-70	-26,505
145 WT	Gas	LEA	-0.6		78	4,029	-47	-26,552
250 MW	Coal	LEA	0.0		149	4,178	0	-26,552
1800 R.E.	Gas	H2O Inj.	1.2		25	4,203	31	-26,521
750 MW	Gas	LEA + 2 St.	-1.8	1.5	569	4,551	-1,035	-25,992
1800 G.P.	Gas	H_2O Inj.	1.9		159	4,710	305	-25,687
750 MW	Oil	LEA + 2 St.	-12.4	2.6	180	4,808	-2,233	-25,434
Pipeline	Gas	H_2O Inj.	3.2		1,370	6,178	4,422	-21,012
500 MW	Gas	LEA + 2 St.	-0.8	7.7	293	6,333	243	-19,824
300 G.P.	Gas	H_2O Inj.	9.3		246	6,579	2,280	-17,544
500 MW	Oil	LEA + 2 St.	-10.6	10.8	99	6,628	-1,056	-17,016
300 R.E.	Gas	H_2O Inj.	13.0		38	6,666	488	-16,528
750 MW	Coal	$Mg(OH)_2$	10.0	19.3	1,273	7,541	12,730	391
HNO_3	New	2 Stage	27.0		114	7,655	3,086	3,477
500 MW	Coal	LEA + FGR	11.7	28.5	568	7,965	6,642	12,306
120 MW	Coal	LEA	35.5		147	8,112	5.214	17,520
36 WT	Coal	LEA	37.7		78	8,190	2,960	20,480
250 MW	Oil	LEA + 2 St.	43.4		48	8,212	162	21,434
250 MW	Coal	LEA + 2 St.	48.3		298	8,361	7,198	28,632
28 WT	Oil	LEA	53.9		67	8,428	3,590	32,222
120 MW	Gas	LEA	58.9		26	8,454	1,550	33,772
300 R.E.	Gas	H_2O Inj.	72.0		3	8,457	219	33,991
HNO_3	Old	2 Stage	77.2		145	8,602	11,186	45,177
250 MW	Gas	LEA + 2 St.	33.3	80.6	59	8,628	1,960	47,297
500 MW	Coal	$Mg(OH)_2$	40.0	102.3	826	8,886	33,040	73,695

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KEY:

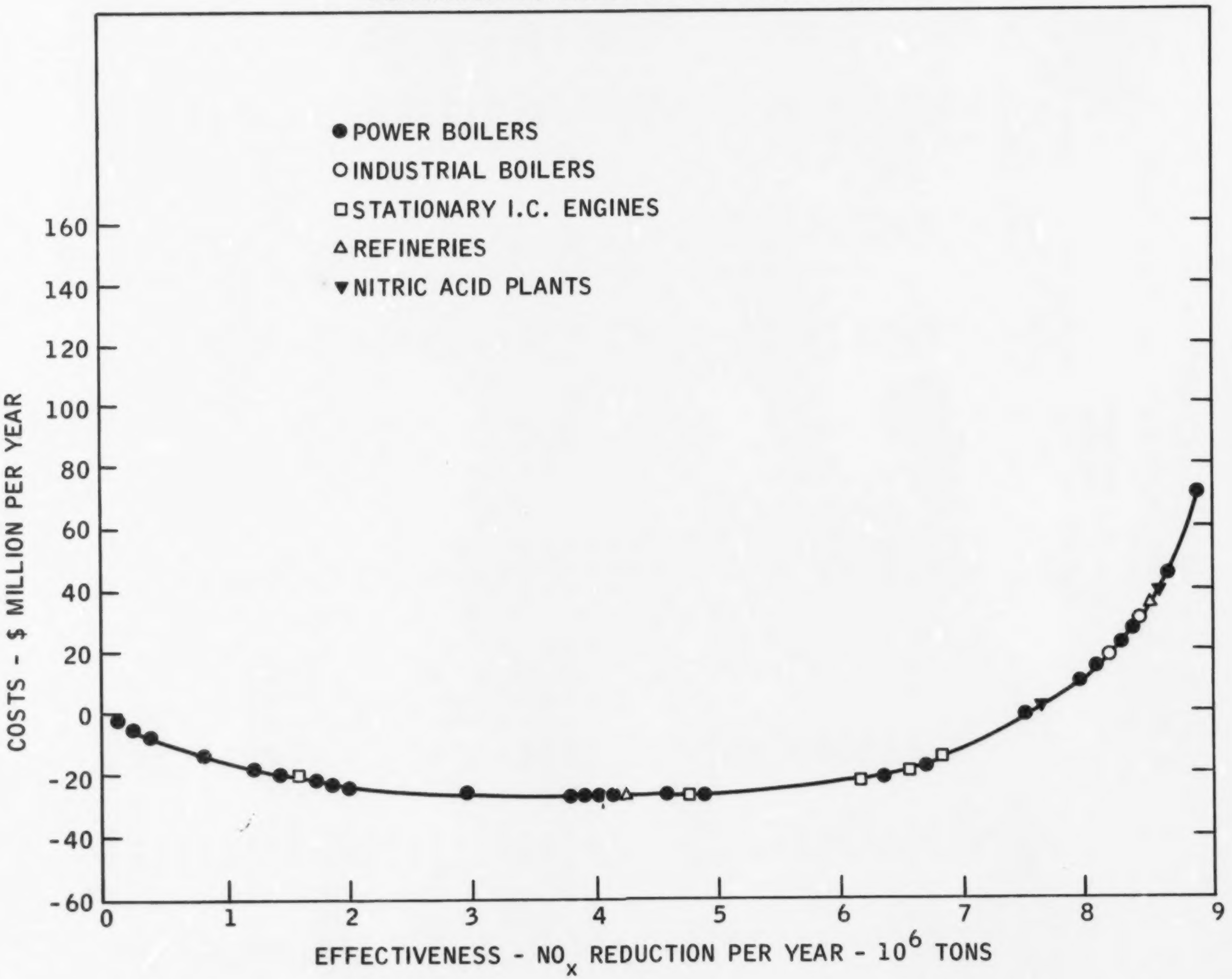
750 MW -- 750 Megawatt Power Boiler
145 WT -- 145,000 lb. st/hr Water Tube Boiler
1800 R.E. -- 1800 HP Refinery Engine
1800 G.P. -- 1800 HP Gas Plant Engine

LEA = Low Excess Air.
2 St. = Two-Stage Combustion.
FGR = Flue Gas Recirculation.
H_2O Inj. = Water Injection.
$Mg(OH)_2$ = Aqueous $Mg(OH)_2$ Scrubbing.

* Incremental substitution costs represent replacement of less costly, but less efficient control methods indicated.

Figure 1-9

COST EFFECTIVENESS PROFILE - NO_x CONTROL
FOR MAJOR UNITED STATES EMISSION SOURCES



On the basis of increasing cost per ton of NO_x removal, as illustrated in Figure 1-9, the control of power boilers has the highest priority followed by those of industrial boilers, stationary internal combustion engines, and nitric acid manufacturing plants. This cost-effectiveness ranking of priorities is in agreement with the "source contribution" of NO_x emission sectors discussed in Section 1.1 and establishes the priority order of R&D plans for controlling stationary NO_x emissions.

1.7 R&D PLANS ON STATIONARY NO_x EMISSION CONTROL

Based on the ranking of stationary NO_x emission sources, and the cost-effectiveness assessment of NO_x control techniques, the 5-year R&D plan program items fall into four major categories:

I. Combustion process studies.

II. Combustion flue gas treatment studies.

III. Non-combustion process studies.

IV. Supporting studies.

Within each category, program items have been divided into basic research and applied R&D requirements. These program items have been ordered into five priority blocks, ranked according to potential accomplishments in terms of NO_x removal. Specific program items in order of priority are listed in Table 1-10.

TABLE 1-10

SUMMARY OF RECOMMENDED R&D PROGRAM ITEMS

Priority	Program Item
1	• Extension of NO_x kinetic model • Definition of NO_x kinetics in combustion processes • Systematic study of combustion modification techniques in power plant boilers • Laboratory studies of problems arising from combustion modification work • Application of basic and applied combustion studies to NO_x control for intermediate and small scale combustion equipment

TABLE 1-10 (cont'd.)

Priority	Program Item
	Engineering studies of best aqueous alkaline scrubbing system
	Evaluation and development of NO_x analytical methods
	Program updating and problem reassessment
2	Measurement of temperature and concentration profiles in combustion equipment
	Determination of basic factors affecting aqueous scrubbing systems
	Pilot-scale studies of major combustion modifications for coal firing
	Engineering, applicability and economic studies of combustion modification techniques for power plants
3	Laboratory studies of improved coal combustion techniques for NO_x control
	NO_x control studies using fluid best combustion
	Evaluation of automotive NO_x emission control techniques for application to stationary I.C. engines
	Definition of design and operating parameter to achieve high scrubber efficiencies required for flue gas scrubbing with sulfuric acid
	Limited testing of equivalent NO/NO_2 absorption in existing prototype SO_2 removal systems
	Study of combustion modification and flue gas treatment techniques that evolve
4	Engineering and economic evaluation of fluid bed combustion for NO_x control
	Continued development of sulfuric acid scrubbing process contigent on achievement of high scrubber efficiencies
	Review and updating of current pollution control programs from standpoint of NO_x control

TABLE 1-10 (cont'd.)

Priority	Program Item
5	• Engineering and economic studies of applicability of NO_x control to specific plants manufacturing or using nitric acid • Review of new chemical process developments • Development of NO_x emission factor data for all sources

The alternative paths in this formulation of the 5-year R&D plans allow the strategy of execution and funding of individual program items to be accomplished within the framework of an "overall" program. This program is made up of different funding levels, depending on the budget available to NAPCA for implementation of the plans.

Rough cost estimates accompany the R&D program items. Based on these estimates, the alternate net R&D costs shown in Table 1-11 have been generated for the 5-year program, excluding the costs incurred by cooperating utility companies, or other owners and operators of industrial equipment.

Table 1-11

Priority and Costs of R&D Program Blocks

	Program Cost, $1,000					
	Years From Start of Individual Program Items					
Priority	1	2	3	4	5	Totals
1	440	670	1,140	950	380	3,580
2	430	575	250	75	0	1,330
3	275	750	1,025	2,450	1,800	6,300
4	200	325	0	0	100	675
5	75	150	125	0	0	350
GRAND TOTAL	1,420	2,470	2,540	3,475	2,280	12,185

Rough estimates of additional cost requirements for participation by power plants range from a minimum total of about $7 million to a high of $19 million, depending on the scope of the test and validation program. An overall contingency of about 25% appears reasonable to allow for program delays, disappointments, and duplication of effort.

The successful execution of the complete R&D program is expected to result in potential reductions of NO_x emissions to pre-1950 levels between the years 1980 and 2000.

2. INTRODUCTION

The role of oxides of nitrogen as air pollutant species first received attention because of their participation in smog-forming atmospheric reactions. Under the influence of solar radiation, oxides of nitrogen, hydrocarbon vapors and atmospheric oxygen interact to form ozone, organic peroxides, and other species such as peracyl nitrates which may result in smog formation, eye irritation, decrease in visibility, crop damage and other effects. The participation of nitrogen oxides in the adverse atmospheric effects observed in the Los Angeles area was first established by Haagen-Smit in 1952 (2-1).

In addition to their role in smog-forming reactions and their consequences, the air pollutant effects of nitrogen oxides *per se* at concentration levels encountered in urban atmospheres are also the subject of ongoing studies by a number of research groups. These toxicological and epidemicological effects of oxides of nitrogen have not yet been clearly established to date.

Only nitric oxide (NO) and nitrogen dioxide (NO_2) are of significance from the standpoint of air pollution. These two oxides of nitrogen are commonly referred to as "NO_x", meaning the sum of the amounts of NO and NO_2 emitted by a variety of sources.

Both stationary and mobile sources emit NO_x into the atmosphere. Prior estimates indicate that roughly one half of the total NO_x pollutants are emitted from stationary sources in the U.S.

The stationary sources of NO_x emissions fall into two major categories: combustion sources and non-combustion sources. As oxides of nitrogen are formed in all fossil fuel combustion processes with air, the contribution of combustion sources to the NO_x emissions in the stationary sector outweigh by a large factor the non-combustion source emissions.

Natural sources also contribute to nitrogen oxide emissions. According to some estimates, on a global basis, the NO_x emissions into the atmosphere from natural sources are about ten-fold the amount of man-made NO_x pollutant emissions (2-2,3). Of course, because of the removal of NO_x from the atmosphere through the natural nitrogen cycle, the order of magnitude of the natural background concentration of NO_x in non-polluted environments is only about 1 ppb. This low concentration level contrasts with average NO_x concentrations of about 40-80 ppb in urban-metropolitan areas. Thus, NO_x pollution is definitely an urban-metropolitan problem, and on a nationwide basis, it should be treated as the summation of such area problems.

To establish the character of the stationary NO_x emission problem, Esso Research and Engineering Company has been conducting under contract to the National Air Pollution Control Administration a systems study of nitrogen oxide control methods for stationary sources. (This study included only man-made sources, thus excluding forest fires which are natural or accidental in character.) The NO_x systems study had the following objectives:

1. Definition of the nature and magnitude of the stationary NO_x problem in the U.S., on a regional basis. This work involved the compilation of NO_x emission inventories for all significant sources from 1950 to date, and making projections and forecasts to the year 2000, taking into account technological, economic and socio-political changes. The stationary NO_x emission inventories and projections were compared with estimates of NO_x emissions from mobile sources.

2. Assessment of existing and potential NO_x control technology. Three broad categories of control techniques have been evaluated: (a) combustion process modification techniques; (b) in-process removal methods of NO_x from flue gases; and (c) other industrial process modifications.

3. Definition of the requirements for a mathematical model of NO_x formation in fossil fuel combustion processes to help guide the design of combustion equipment producing low NO_x emissions. A first-generation mathematical model has been formulated and used to determine the directional effects of changes in parameters on NO_x formation in natural gas combustion processes.

4. Analyses of cost-effectiveness (for various degrees of control), based on the technical and cost assessment of existing and potential NO_x control methods. (The cost-effectiveness analyses were made to guide the formulation of R&D programs on NO_x control, and should not be misconstrued as recommendations for the implementation of techniques prior to the R&D work.)

5. Recommendations of alternate 5-year R&D plans for NAPCA's Phase II program on stationary NO_x emission control.

This report summarizes work done and the conclusions reached in the Phase I portion of the work funded by NAPCA in this area.

2.1 REFERENCES

(2-1) Haagen-Smit, A. J., "Chemistry and Physiology of Los Angeles Smog", Ind. Eng. Chem., 44(6):1342-6, 1952.

(2-2) Robinson, E., and Robbins, R. C., "Gaseous Atmospheric Pollutants from Urban and Natural Sources", Air Poll. Control Assoc. Preprint No. 69-155.

(2-3) Robinson, E. and Robbins, R. C., "Sources, Abundance and Fate of Gaseous Atmospheric Pollutants", SRI Project PR-6755, Report for American Petroleum Institute, February 1968.

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3. CHARACTERIZATION OF THE NO_x EMISSION PROBLEM FOR STATIONARY SOURCES

In this section the nature and magnitude of the NO_x emission problem from stationary sources in the United States is defined in sufficient depth to be useful in establishing required control technology R&D. Definition of the problem includes identification of NO_x emitters, determining their magnitude and distribution for the period 1950 to the present, and making projections of their number and characteristics to the year 2000. Projections have been made considering technological trends, changing energy sources due to availability and economics as well as socio-political factors. Major emphasis has been on current emissions, and the years 1980 and 2000. Detailed, accurate data for the recent past provide a solid basis for extrapolation to the year 1980 as a convenient base point, since it is long enough away to depend upon an estimate of future trends but not so distant as to be very uncertain. The year 2000, however, is far enough in the future so that fundamental technological changes can take place, and it is necessary to consider morphological analysis and technological forecasting in addition to extrapolation of past and current trends. Thus, some current emission sources such as household coal-burning furnaces will almost surely be eliminated by the year 2000, while new sources such as magnetohydrodynamic (MHD) generation might well be an important source for electricity.

NO_x pollution in urban air is important chiefly because it plays a key role in the development of Los Angeles type smog. This photochemical smog is a mixture of gases and particulates which develops in sunlight over a period of hours through complex reactions between hydrocarbons and nitrogen oxides. If there is not enough wind to blow it away, this photochemical smog reduces visibility and causes eye irritation. During severe episodes, it can cause nose and throat irritations and other problems.(3-1)

Air pollution is a complex problem, since both its nature and importance will vary from area to area, from season to season, and from hour to hour. Rapid urban growth has resulted in concentrating a large proportion of the population within a relatively small land area (more than half of the U.S. population lives on 19% of the land(3-2)) and also in changing meterological conditions over the city areas.(3-3) Major variables affecting the nature and importance of the air pollution problems at any one time and place are: type and amount of pollutants, wind speed and direction, air temperature change with height, amount of sunlight, precipitation, topography, and population density.

3.1. SOURCES OF NITROGEN OXIDES

Nitrogen oxides are formed under all common types of combustion processes, and from some non-combustion processes such as nitric acid manufacture or by various biological reactions in nature. Man-made NO_x is largely a by-product from fossil fuel combustion with over one-half emitted from stationary sources and the remainder from mobile sources such as automobiles, and diesel railroad engines. This report is primarily concerned with man-made stationary sources such as power plants, industry and household. Emissions from mobile sources are treated at length in the NAPCA document, "Control Techniques for Carbon Monoxide, Nitrogen Oxides, and Hydrocarbon Emissions from Mobile Sources."

The NO_x formed in combustion comes from two distinct sources. With methane or any pure hydrocarbon fuel, it comes entirely from the high temperature reaction of nitrogen and oxygen in air to form NO. Nitrogen compounds in fuels also lead to NO_x. With ammonia as the fuel the product is very high in NO, with some nitrogen (and water), and this is the chief commercial starting point for the manufacture of nitric acid from NO. Other nitrogen containing fuels, such as coal or fuel oil, can produce some NO_2, NO and possibly nitrogen, depending upon the reducing nature of the flame.

In combustion processes, as will be discussed in Section 4, the main factors in NO_x formations are: the flame temperature, the length of time the combustion gases are maintained at that temperature, and the amount of excess air present in the flame. Small combustion units operating under relatively mild conditions give an exhaust gas containing only small amounts of NO_x, such as the 10 ppm or less formed in a typical domestic gas-fired water heater. This range rises rapidly with combustion severity and may reach 500 to 1000 ppm or more in a power plant steam boiler.

The non-combustion sources of NO_x due to the activities of man are relatively small, about 2% of total NO_x. They arise mainly from the manufacture and use of nitric acid. In general, the NO_x concentrations arising from these sources are much greater than those of combustion sources and they often form highly visible red-brown emissions.

There appears to be little doubt that NO_2 is removed from the atmosphere through hydrolysis to nitric acid, which is then precipitated out as nitrates in rainfall or in dusts. The residence time of NO_2 as such in the atmosphere is only a few days(3-5). NO_x is an essential part of the natural nitrogen cycle of organic growth, decomposition into the atmosphere, and return to soil as natural fertilizer. The natural cycle is estimated to produce a worldwide NO_2 emission of about 500×10^6 tons per year(3-6). The air pollution caused by NO_x emissions tends to become progressively worse where there are the most people and the heaviest demands for industrial combustion energy(3-1). The concentration of NO_x in U.S. urban areas averages 40-50 ppb(3-8), strikingly greater than the background level of 1 ppb. Thus, it is man-made sources which create the problem of control.

The four-part report entitled "Emissions of Oxides of Nitrogen from Stationary Sources in Los Angels County"(3-9) has been a useful guide for the initial evaluation of emission sources. This study indicated the following breakdown of sources in Los Angeles County:

Table 3-1

Stationary NO_x Sources in Los Angeles County	% of Total
Fossil Fuel Electric Power Plants	44
Other Steam Boilers	19
Stationary Internal Combustion Engines	15
Refinery Heaters	9
Domestic Gas Appliances	6
Glass Furnaces	2
Steel Furnaces	1
All Other Sources	4
Total	100

As shown in Table 3-1, 44% of the stationary emissions in Los Angeles were due to electric power generation, while another 19% resulted from non-power boilers. Although the national emission pattern was not expected to match the Los Angeles results exactly, subsequent studies have indicated similar general patterns.

The problem of obtaining information on NO_x emissions, and on fuel usage by type and consumer sector was handled by a detailed review of the pertinent literature in combination with field survey contacts. These information sources were also utilized to obtain the required background on socio-economic and technological trends.

In the field survey, contacts have been made with governmental agencies at the federal, state, county and local levels, and with centralized institutional sources. To the degree warranted by the contribution of specific emission sectors to the overall NO_x emission problem, personal contacts have been established with individual experts in power generation and other industrial processes.

Since fossil fuel fired power plants have been identified as the largest single source of stationary NO_x emissions, a detailed survey was devised to obtain detailed and up-to-date information on steam electric plant operations and design features.

Similarly, major industrial, commercial and household sectors were surveyed using a combination of statistical data, published information and field survey contacts. This type of analysis has been applied to major industrial sectors, such as the petroleum and primary metals industries, which generate NO_x emissions through the combustion of fossil fuels, as well as to non-combustion sources such as nitric acid manufacturing plants and chemical processing.

Figure 3-1 shows our estimate of NO_x emissions from stationary sources in the U.S. for 1968 by broad types of use. The largest NO_x producers outside of electric power plants (and automobiles) are the natural-gas driven compressors for oil and gas pipelines and gas plants. These are largely non-urban sources, discussed in detail in Section 3.1.2. below. A comparison between coal, oil, and gas for ordinary use in power plants or boilers is given in Table 3-2. This lists average emission factors on a uniform BTU basis, for ready comparison. Wide variations from these data are to be expected in individual units, as discussed in Section 3.2. of this report. Coal and natural gas each account for about 40% of all NO_x from U.S. stationary installations, with oil accounting for about 15%.

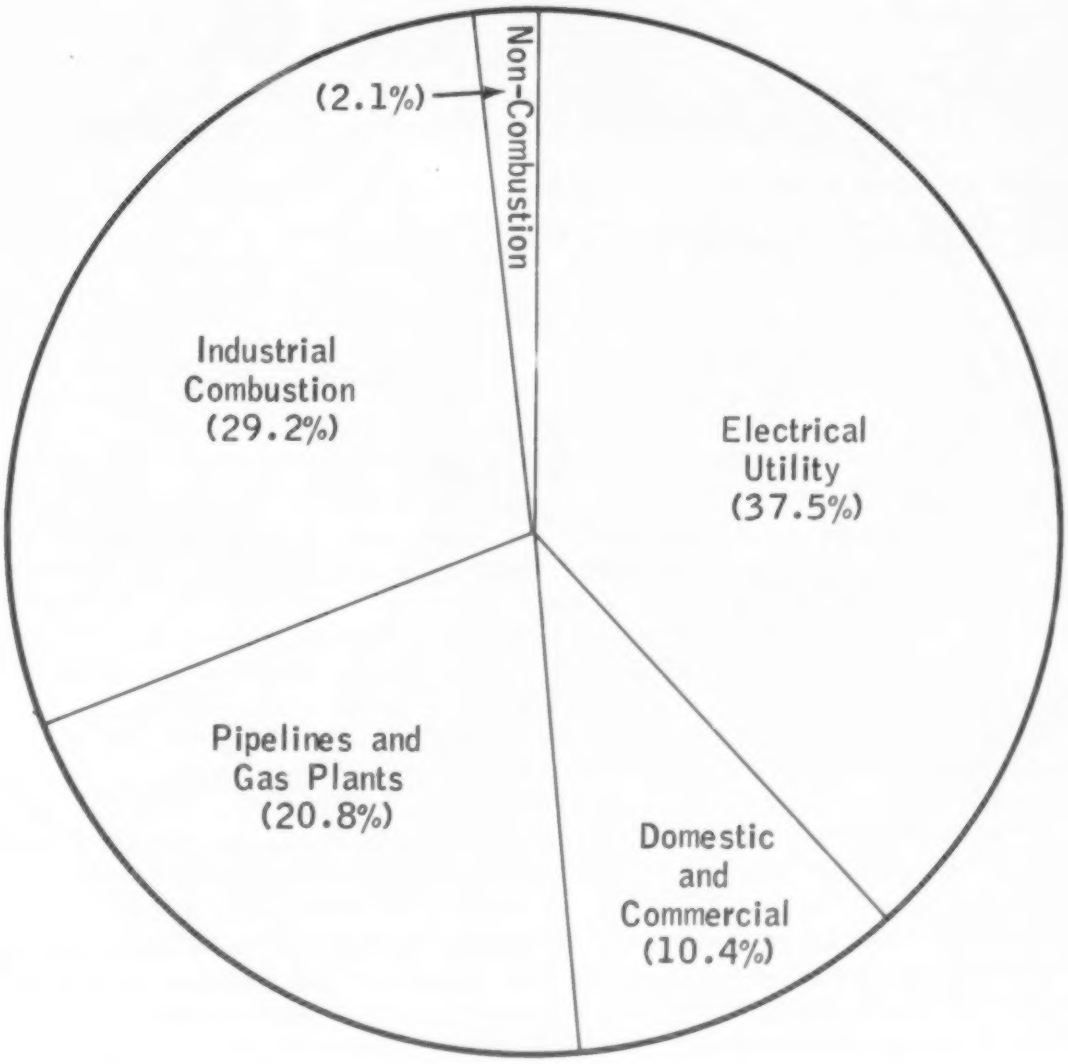
Table 3-2

Comparison Between Coal, Oil, and Gas on Equivalent BTU Basis(3-10)

	Average NO_x Emissions in Boilers and Power Plants (Pounds $NO_x/10^9$ BTU)		
Fuel	Household and Commercial	Industry	Electric Power Generation
1. Natural Gas (1,046 BTU/cu.ft.)(3-11)	111	205	373
2. Fuel Oil (149,966 BTU/gal)(3-11)	80-480	480	693
3. Coal (11,867 BTU/pound)(3-11)	337	842	842

Figure 3-1

TOTAL NO_x EMITTED IN THE U.S.
FROM STATIONARY INSTALLATIONS, 1968



NO_x, Estimated Tons*, 1968	Type of Installation
3,600,000	Electrical Utility
2,800,000	Industrial Combustion
2,000,000	Pipelines and Gas Plants
1,000,000	Domestic and Commercial
200,000	Non-Combustion
9,600,000	U.S. TOTAL

*Calculated as NO_2.

3.1.1. Steam Electric Generation

As shown in Figure 3-1, steam electric power generation is estimated to account for about 38% of NO_x emissions from stationary sources in 1968. Since electric power generation has grown very rapidly in the past and is expected to approximately double in each ten year period in the future, it has been given special attention in this report. Tables 3-3 and 3-4 below give past and future trends of fuel consumption and electric generation:

Table 3-3

Trends in Power Plant Consumption of Fossil Fuels

	1955	1965	1980 (3-13)	2000 (3-13)
Natural Gas - 10^9 cu ft(3-14)	1,153	2,318	3,300	4,240
Fuel Oil - 10^6 Bbl	82	119	250	370
Coal - 10^6 Tons	144	245	445	1,120

Table 3-4

Trends in Electricity Generated From Fossil Fuels
Hydropower and Nuclear Power(3-12)

Fossil Fuel Plant - 10^9 KWH	431	857	1,770	3,970
Hydro Power - 10^9 KWH	116	195	320	500
Nuclear Power - 10^9 KWH	0	4	720	5,530
Total Generation-10^9 KWH	547	1,056	2,810	10,000

Of the known recoverable energy reserves in this country, about 93% are in the form of coal according to both the Bureau of Mines(3-15) and the Cambel(3-16) estimates. However, data on reserves can be misleading because much of the readily available coal is of high sulfur content, especially that located near the major eastern markets. In addition, there may be a shortage of available production capacity developing(3-17).

The U.S. Geological Survey estimated total proven and unproven reserves of natural gas reserves at 1,700 billion MCF, or about 100 years supply at the present rate of use(3-18). However, the unproven reserves are uncertain and may involve higher costs. Imports of liquified natural gas may become more important in the future, making the United States less dependent upon North American reserves(3-14)

Current estimates of ultimate United States crude-oil reserves are in the range of 500 billion barrels(3-19) with about 92 billion of future recoverable reserves. However, about 85% of the residual fuel oil used in the east coast markets comes from Caribbean refineries. Future additional sources of oil for the United States include the potential supplies in the oil shale formations of Wyoming, Colorado, and Utah; the tar sands in Canada and the United States and the possible liquefication of coal.

As shown in Table 3-3, hydro-generation is expected to decrease in relative importance between 1980 and the year 2000. Nuclear generation, on the other hand, is forecast to increase rapidly in the future. By the end of 1968 about 90 nuclear plants totaling about 65 thousand megawatts of generating capacity were on order, under construction or operating.(3-20). Known reserves of nuclear fuel are available through the 1970's and a rapid expansion of private prospecting is underway(3-21). The economic development of breeder reactors would drastically increase the value of reserves and there is considerable research by private and governmental agencies being conducted to this end.

Since power plants are the largest single source of NO_x emissions, detailed plans have been developed to obtain information on this industry. The centralized institutional and governmental agencies that have been surveyed by personal visits include the Edison Electric Institute, Electric World Magazine, Federal Power Commission, American Boiler Manufacturers Association, National Oil and Fuel Institute and the Bureau of Mines. Through these visits, literature studies, and discussions with experienced company engineers, we have developed the Steam-Electric Plant Survey Questionnaire-Appendix 3-1, Steam-Electric Plant Survey Instructions-Appendix 3-2 and Steam-Electric Plant Questionnaire, Example-Appendix 3-3. The questionnaire has been divided into Section I-Boiler Information, Section II-Two Stage Combustion Information Sheet and Section III-Peak Shaving Units (Gas Turbines-Internal Combustion Engines). The final details of the questionnaire were established through detailed discussions with representatives of the electric utility industry.

Nineteen of the largest utilities in the nation were selected to receive this questionnaire. Factors used in evaluating which companies were to be included in the sample were: size (net power generated), type of fuel used, geographic location, and availability of emission inventory data by Air Quality Control Region. Federal Power Commission data have been recorded for boilers on steam pressure, maximum steam rating, initial year of operation, manufacturer and type of firing. Data available on peak shaving units (gas turbines and internal combustion engines) include unit number, nameplate rating, year installed, manufacturer, fuel consumption at full load, exhaust gas temperature and inlet gas temperature. All of the other data on the questionnaire have been obtained by contacting the individual companies. Thirteen companies completed the questionnaire.

The questionnaire provided relatively little new NO_x emission data, especially for coal burning. Boiler design and operating data for the boilers with reported NO_x measurements are summarized in Appendix 3-5. As will be discussed in Section 3,2., considerable additional research is needed to provide accurate emission rates for the multitude of boilers in use today.

The large watertube boilers in public utility power generating stations (see boiler outlines in the Appendix) are all of custom design with only a few identical designs in existence. Except for supercritical boilers having special configurations, most large power station boilers are of the radiant type illustrated in the Appendix. This type of boiler ranges in size from perhaps 300,000 to 7,000,000 pounds of steam per hour. The radiant boiler has a relatively large water cooled furnace which in modern units is generally pressurized, with superheat and reheat surfaces which may be of both radiant and convection types, economizers, and either tubular or rotating Ljungstrom type air heaters.

Radiant boiler designs differ from one another chiefly in the type of firing used. Boilers serving turbine generators up to 300 MW in size are fired by multiple burner installations which may be located in the front wall firing horizontally, in the corners firing in a tangential pattern, firing vertically downwards, firing downwards on an angle in the turbo-furnace, or in special cyclone burners. It is difficult to find space for the large numbers of burners needed in radiant boilers serving generators over 500 MW in size, and these larger boilers are usually fired with burners located in both the front and rear walls, horizontally opposed, or firing tangentially as previously described.

Coal, oil and gas are the usual fuels fired in boilers. Special fuels such as lignite, liquified petroleum gas, distillate fuel oil, refuse, and special chemical wastes or byproduct fuels are also used, but the quantities consumed are relatively small. For the purposes of this report, coal, heavy fuel oil and natural gas are considered the major fossil fuels.

3.1.2 Petroleum and Natural Gas Industries

This section covers oil and gas production, pipeline transportation, gas plant operation and petroleum refining. Transportation on tankers, barges, trucks, and rail is not covered here because these are mobile sources.

Oil and gas production operations which are major power consumers include drilling, oil well pumping, gathering, gas and water injection to the producing formation, and oil dehydration. Gas plant operations include removal of impurities such as water and sulfur compounds, and recovery of valuable natural gas liquids such as ethane, propane, butane, and natural gasoline.

In petroleum refining, crude oil is converted into salable products in the required volumes. A simplified flow sheet for a refinery appears in Figure 3-2. Crude oil is charged to an atmospheric pipestill where light products are taken overhead and light catalytic reforming feed, raw gasoline, kerosene, middle distillate and heavy gas oil are taken as side-stream products. The reduced crude is charged to a vacuum pipestill where heavy gas oil, lube stocks and residuum are cut.

NO_x emissions in the petroleum and natural gas industries result from the combustion of fuel in process heaters and boilers, and from internal combustion engines for driving compressors and electric generators. NO_x is also released from catalytic cracking regenerators and from CO boilers.

Oil and gas production, gas plants, and pipeline stations are usually remote from heavily populated areas so that the emissions do not contribute substantially to NO_x levels in populous areas. Petroleum refineries, however, are often located in or near populous areas.

Estimates of the amounts of NO_x emitted from petroleum and natural gas operations in the year 1967 are shown in Table 3-5.

Diesel oil consumed in oil and gas production was taken as residual plus diesel fuel oil consumed in "oil-company use" (3-19) minus fuel oil "consumed at refineries" (3-22). All diesel oil in oil and gas production was assumed to be used in diesel engine drivers, the disposition with the highest emission factor. Gas consumed in oil and gas production was estimated by subtracting gas used in gas plants plus estimated shrinkage from gas field use (3-23).

In the refining sector, the numbers shown for gas include natural gas, liquified petroleum gas (LPG), and refinery gas, converted to natural gas on the basis of heat of combustion (3-22). Oil consumption includes acid sludge.

FIGURE 3-2

PROCESSING PLAN FOR COMPLETE MODERN REFINERY

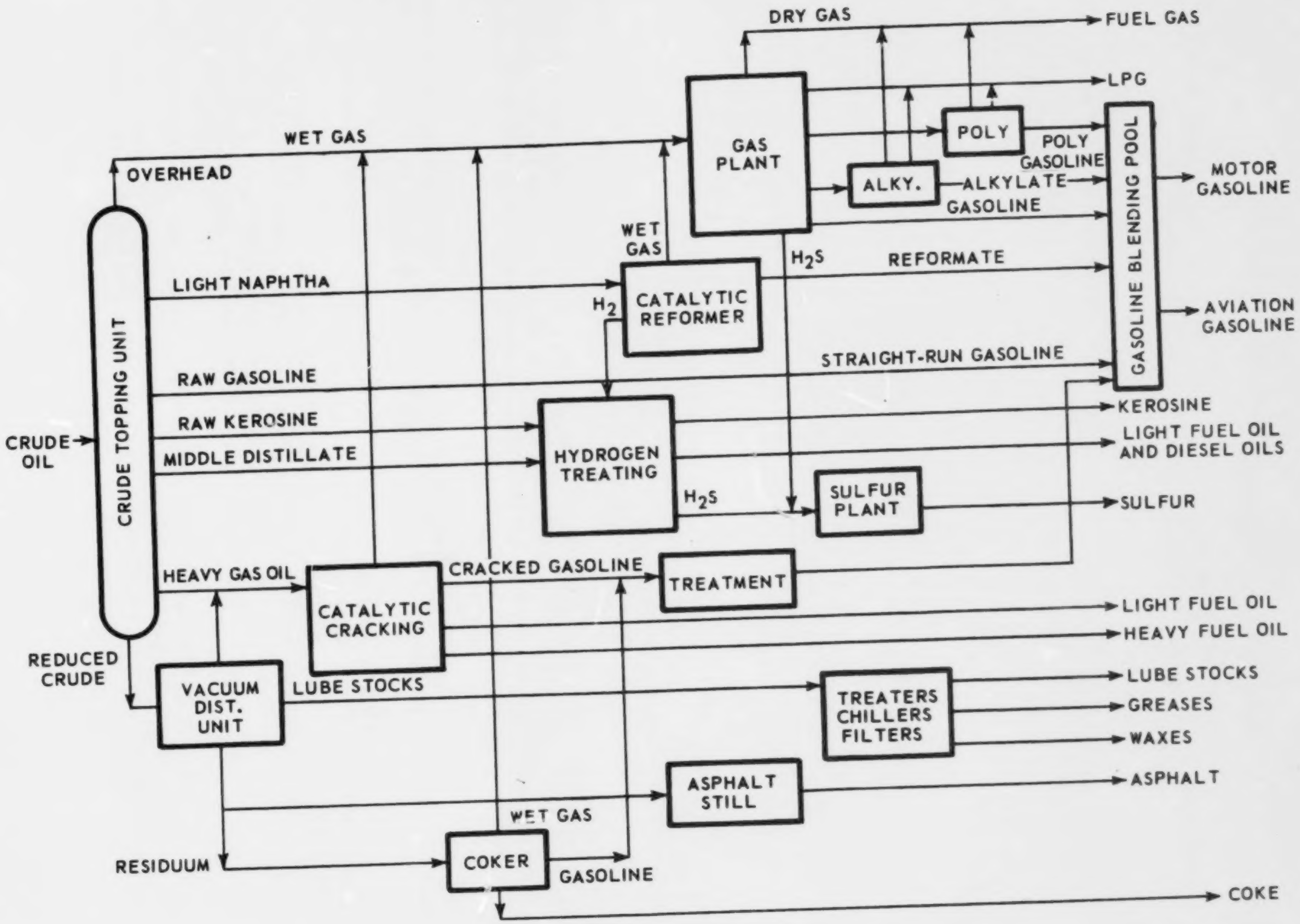

DRY GAS
FUEL GAS
LPG
WET GAS
OVERHEAD
GAS PLANT
POLY
POLY GASOLINE
ALKY.
ALKYLATE
GASOLINE
GASOLINE BLENDING POOL
MOTOR GASOLINE
AVIATION GASOLINE
WET GAS
H$_2$S
REFORMATE
LIGHT NAPHTHA
H$_2$
CATALYTIC REFORMER
STRAIGHT-RUN GASOLINE
RAW GASOLINE
RAW KEROSINE
MIDDLE DISTILLATE
CRUDE OIL
CRUDE TOPPING UNIT
HYDROGEN TREATING
KEROSINE
LIGHT FUEL OIL AND DIESEL OILS
H$_2$S
SULFUR PLANT
SULFUR
HEAVY GAS OIL
CATALYTIC CRACKING
CRACKED GASOLINE
TREATMENT
LIGHT FUEL OIL
HEAVY FUEL OIL
REDUCED CRUDE
VACUUM DIST. UNIT
LUBE STOCKS
TREATERS CHILLERS FILTERS
LUBE STOCKS
GREASES
WAXES
ASPHALT STILL
ASPHALT
WET GAS
RESIDUUM
COKER
GASOLINE
COKE

Table 3-5

NO_x Emissions from Petroleum And Natural Gas Operations, 1967

	Fuel(1) Consumption	Emission(2) Factor	NO_x		
			PPM Range	Thousand Tons/Yr.	
Oil and Gas Production					
Gas					
Heaters and Boilers	495(a)	0.2 (c)	25-200	50	
Gas Engines	124(a)	0.77(d)	250-2500	48	
Oil					
Diesel Engines	7.3(b)(g)	9.3 (e)		34	
Production Subtotal					132
Gas Plants					
Gas					
Heaters and Boilers	247(a)	0.19(c)	25-200	24	
Gas Engines	260(a)	4.3 (d)	1000-3500	561	
Gas Turbines	15(a)	0.2 (f)	50-200	2	
Gas Plant Subtotal					587
Pipelines					
Gas					
Gas Engines (h)	436(a)	7.3 (d)	1500-3500	1596	
Gas Turbines	140(a)	0.2 (f)	50-200	14	
Pipeline Subtotal					1610
Refining					
Gas					
Heaters and Boilers	1656(b)	0.21(c)	25-200	173	
Gas Engines	40(b)	4.35(d)	1000-3500	87	
Gas Turbines	54(b)	0.2 (f)	50-200	5	
Oil					
Heaters and Boilers	39.7(b)	2.8 (e)	50-400	56	
Other				9	
Refining Subtotal					330
Total - Petroleum and Natural Gas					2659

(1) Oil Consumption as million barrels/year.
Gas Consumption as billion standard cubic feet/year.

(2) Oil emission factors - pounds NO_x/barrel.
Gas emission factors - pounds/thousand standard cubic feet.

(a) Reference (3-23)
(b) Reference (3-22)
(c) References (3-24,25)
(d) Reference (3-26)
(e) Reference (3-10)
(f) See Table 3-9
(g) Reference (3-19).
(h) Gas-fired reciprocating piston engines.

Allocation of gas plant fuel between heaters and boilers, gas engines, and gas turbines is based on a survey of sources of NO_x emissions in the oil and gas industries made in this study. Allocation of pipeline fuel between "gas engines" and "gas turbines" is based on capacities indicated by Pipe Line Industry (3-27). Allocation of gaseous fuels to the various users in refineries is based on industry survey (3-24, 3-25), which is summarized in Appendix 3-7.

Emission factors for gas fired heaters are derived from Figure 3-3. This relationship between NO_x production rate and fuel firing rate is based on emission data obtained in the petroleum and natural gas survey. Emission factors for diesel engines and oil fired furnaces are taken from Duprey (3-10). Emission factors for gas engines are based on Figure 3-4, which is reproduced from the studies of Mills, et al. (3-9). Emission factors for gas turbine engines are from Table 3-9, below. Furnace and engine sizes in the various applications are based on the survey of the petroleum and natural gas industry (3-24, 3-25).

Other emissions in refining include NO_x produced in catalytic cracking regenerators (3000 tons per year), and NO_x from carbon monoxide burned in CO boilers (6000 tons per year). These emissions from catalytic cracking regenerators result from cracking 4190 thousand barrels of fresh feed per day (3-28), at an emission rate of 4.2 pounds NO_x per thousand barrels (3-9). There are 75 CO boilers in the United States, each of which emit an estimated 21 pounds per hour of NO_x.

Cat-cracking regenerator emission factors are derived from the data reported by Mills, et al. (3-9). The factors reported by Duprey (3-10) were based on earlier data from Los Angeles (3-29) which were superseded by the later measurements (3-9). CO boiler factors are based on recent tests by Union Oil Company (3-30).

Data on NO_x emissions from the catalytic cracking regenerators and from CO boilers are apparently conflicting and difficult to interpret. The available data are summarized in Table 3-6, which indicate a range of 0 to 394 ppm of NO_x for catalytic cracking regenerator stack gas, and 17 to 645 for CO boilers.

Coke burning in catalytic cracking regenerators is carried out at well below stoichiometric air requirements, at bed temperatures in the 1100-1250°F range. The CO/CO_2 ratio in the stack gas is about 1/1. While local temperatures could be higher than bed temperature, fixation of nitrogen from the atmosphere is not to be expected. This draws attention to the possibility that nitrogen in the coke may be the predominant contributor to NO_x formation. Examples of the role of oxidation of nitrogen in the fuel in NO_x formation under mild combustion conditions are discussed in Section 4.2.

FIGURE 3-3

NO_x EMISSIONS FROM REFINERY FURNACES

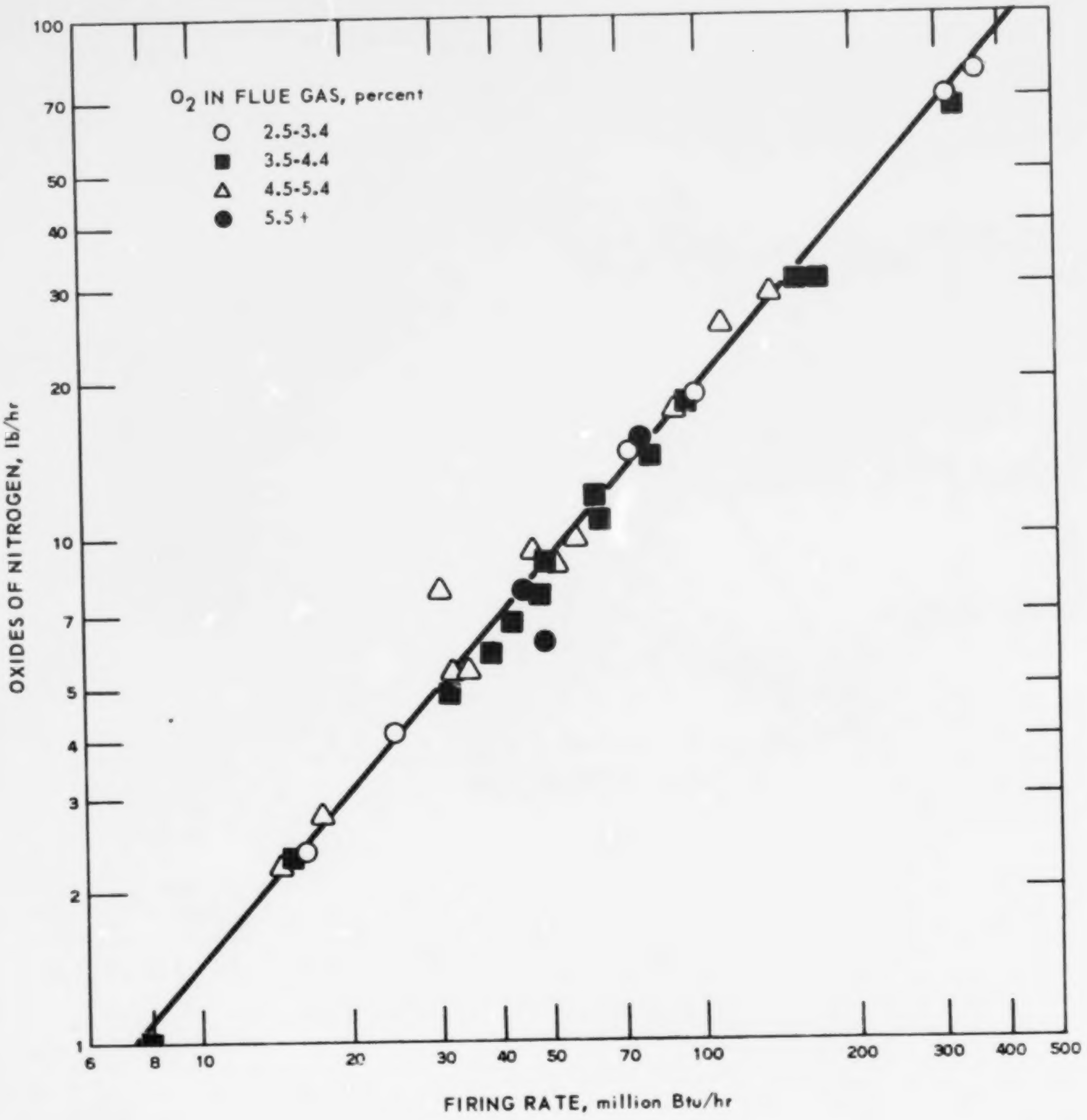
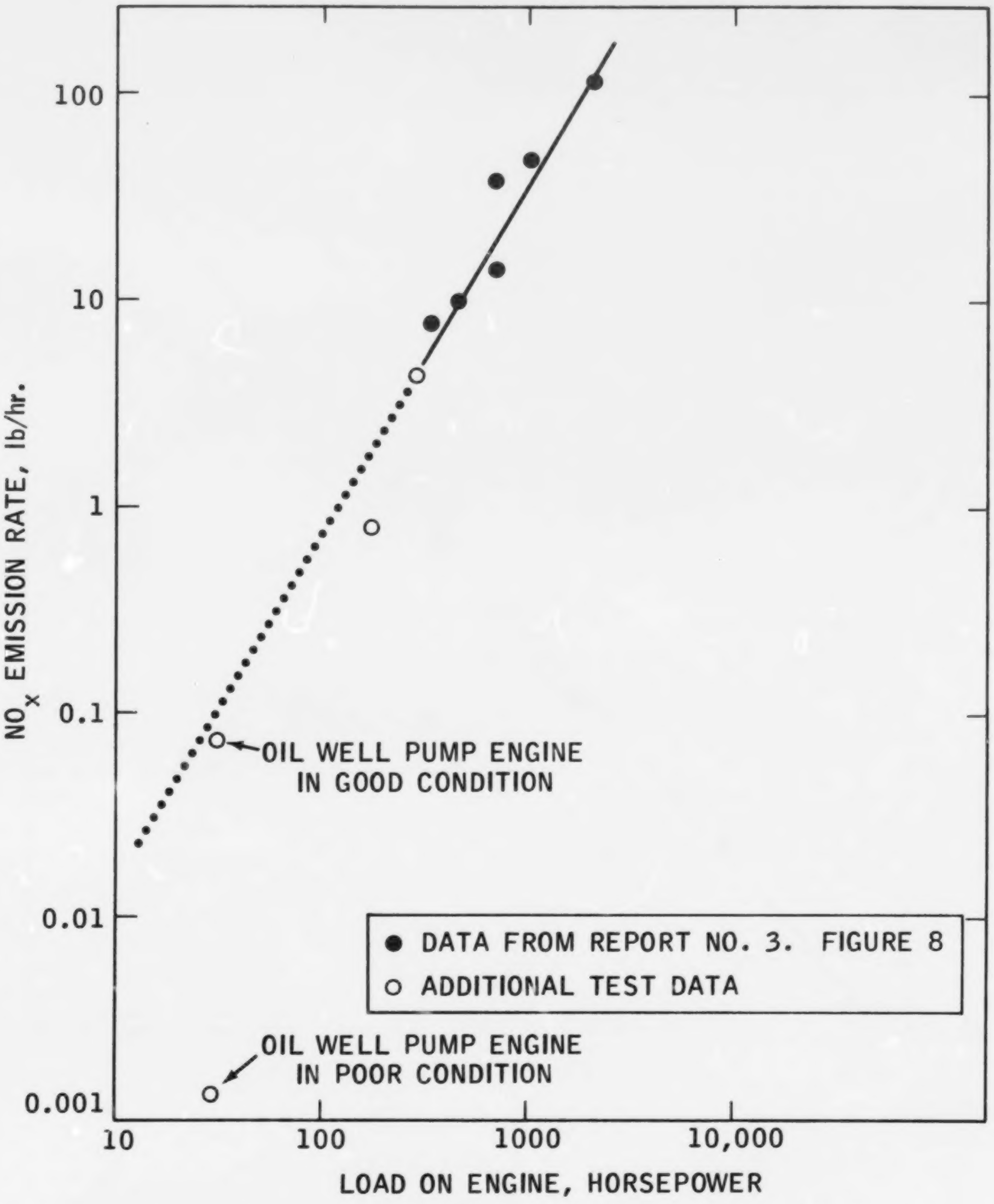


Figure 3-4

NO_x EMISSIONS FROM STATIONARY INTERNAL COMBUSTION ENGINES*



* The dotted part of the line represents the curve from Fig. 8, Report No. 3, extrapolated downward (3-9).

As will be discussed in Section 4, organically bound nitrogen can be oxidized to NO_x. Catalytic cracking feedstocks contain varying amounts of nitrogen, averaging about 0.06% by weight. However, California crudes are notorious sources of high nitrogen catalytic cracking feedstocks which contain as much as 0.4% or more nitrogen. Rough calculations indicate that catalytic coke from California crude sources could contain 2% or more of nitrogen, since an estimated 20-50% of feedstock nitrogen appears in the coke, and coke yields range roughly between 3 and 6% by weight on fresh feed. Thus, it is likely that catalytic cokes from high nitrogen feedstocks contain at least as much nitrogen as coals, which contain between 1 and 2% nitrogen.

A possible source for the higher NO_x levels reported for catalytic cracker regenerator flue gas is the oxidation of the nitrogen in catalytic coke. Lower NO_x levels may reflect lower nitrogen coke produced from low nitrogen gas oils.

Due to the low heat of combustion of catalytic cracker regenerator stack gas, combustion temperatures in CO boilers are lower than in conventional boilers. When auxiliary fuel is minimized, the NO_x in the CO stream from catalytic cracking is not expected to re-equilibrate at the low combustion temperatures, and thus may pass through the CO boiler virtually unchanged.

It should be emphasized that the hypothesis advanced above is based on scant data. Available data include no information on crude source, or nitrogen level of cat cracker feed; regenerator or CO boiler temperatures, and other factors.

Additional data are required to prove or disprove these theoretical considerations and to determine how best to reduce NO_x emissions, if required. One possibility is to hydrotreat catalytic cracking feed for nitrogen removal. The latter solution would also reduce sulfur oxides emissions both from catalytic cracking and the combustion of fuel products, as well as improve catalytic cracking yields. The economics depend upon the balances between these credits and the substantial costs for severe hydrogenation required for denitrogenation.

Emission factors for gas engines are not firmly established. In Figure 3-4, the high values for the large engines reported by Mills, et al. are believed to reflect lean combustion mixtures, supercharging, low speed and other factors which favor high NO_x emissions (Section 3.1.3). The values for smaller engines reported by Mills et al. are probably for naturally aspirated engines operated at higher speed with rich combustion mixtures, factors

TABLE 3-6

NO_x EMISSIONS FROM CATALYTIC CRACKING REGENERATORS AND CO BOILERS

	Source of Data	NO_x Emissions ppm	
		Range	Average
Catalytic Cracking Regenerators	(3-29)	0-394	89
	(3-9)	0-37	16
CO Boilers	(3-29)	191*	191*
	(3-9)	90-155	113
	(3-30)	17*	17*
	(3-25)	165-210	185
	(3-25)	645*	645*

* Only one value reported.

favoring low NO_x. The position of the points on the plot probably reflect these factors, not size *per se*. Thus, the correlation of Figure 3-4 is used as a means of interpolation in estimating emissions. Extrapolation of the correlation for engines larger than 2000 HP, the largest size tested, was avoided, and emission factors derived for the 2000 HP engine were applied to larger engines.

It should be emphasized that only meager data are available for gas engines, and the emission factors may not be truly representative. The use of Duprey's gas engine emission factor, based on tests of engines averaging about 350 HP (3-26) would result in estimated pipeline and gas plant emissions of only 200 thousand and 140 thousand tons per year of NO_x.

NO_x emissions from the petroleum and natural gas industries as a percentage of total NO_x from all sources in the U.S. are shown in Table 3-7, for the year 1967.

TABLE 3-7

NO_x EMISSIONS FROM U.S. OIL AND GAS INDUSTRY, 1967

	NO_x Emitted, Tons/Yr.	% of Total NO_x Emissions
Oil and Gas Production	132,000	0.9
Gas Plant	587,000	3.8
Pipeline	1,400,000	9.3
Refining	330,000	2.2
Total	2,659,000	16.2

3.1.3 Other Combustion Sources

Stationary engines, solid waste incinerators, metallurgical processes, kilns and glass furnaces, NO_x emissions will be discussed in this section.

3.1.3.1 Stationary Engines

As has been pointed out in previous discussions, the combustion of fuels with air results in the formation of oxides of nitrogen. These species are formed by the direct combination of molecular nitrogen and oxygen in the flames. The thermodynamics and kinetics of the reaction indicate that the control of NO formation must consist of lowering flame temperatures, limiting the availability of the reactant (oxygen and nitrogen), or control of net reaction rates.

The stationary engine population in the United States is made up of both reciprocating piston engines and gas turbines. The reciprocating piston engine population is distributed (3-31) is as follows:

TABLE 3-8

STATIONARY RECIPROCATING PISTON ENGINES, U.S. 1967

	Fuel	% of Total(a)
Full Diesel	Liquid Fuel Oil	15
Dual Fuel	Liquid or Gas	19
Spark-Ignition Gas	Gas	66

(a) It is estimated 85% of these engines are supercharged (3-32) and about 1% are the pre-combustion chamber type (3-31).

No figure of the power capabilities of the total installed piston engine population has been located. However, from distillate fuel oil consumption in "industrial and other" stationary engine applications (3-33), it is estimated the total current piston engine capacity may approximate 70 million HP (assumes 2/3 of the engines are gas fired, service factors of 0.6 for prime movers in manufacturers installations, 0.2 in electric utility uses, and a fuel consumption of 0.4 lbs fuel/brake HP/hour). This is probably low because some large oil fueled diesel engines undoubtedly use heavy fuel oil which would not appear in the distillate fuel figures.

The NO_x emission characteristics of various types of piston engines are listed in Table 3-9. It should be emphasized that these data are based on experiments in relatively small engines (e.g., truck types, say about 200 HP) and there may be some question about extrapolating the numbers to large engines. However, it is believed the data do provide a valid indication of the effect of the various engine variables. The data on the gas turbine engine are from conventional aircraft turbojet types. The following preliminary tentative conclusions can be made:

- Turbocharging a piston engine may double NO_x production.
- The precombustion chamber piston engine seems to produce about 1/3 as much NO_x as a direct injection, piston engine.
- An oil-fired turbojet engine may produce about 0.1 as much NO_x as an oil-fired, direct injection diesel engine.

TABLE 3-9

ESTIMATED STATIONARY ENGINE DISTRIBUTION U.S. - 1969

No.	Reciprocating Engine	Supercharged	Fuel	Estimated Total HP (millions)	Reference	NO_x Emissions Lb. NO_x/Lb. Fuel	NO_x Emissions Lb. $NO_x/10^6$ BTU
1.	Diesel-Precomb. Chamber	Yes	Oil	0.7	(a)	(0.02)	(0.9)
2.	Diesel-Precomb. Chamber	No	Oil	0.1	(3-34)	0.007-0.010	0.38-0.55
3.	Diesel-Direct Injection	Yes	Oil	14	(3-35)	0.07	3.8
4.	Diesel-Direct Injection	No	Oil	2	(3-36,37)	0.021-0.047	1.2-2.6
5.	Gas Engine (Spark Ig.)	Yes	Gas	45	(a)	0.16	8.0
6.	Gas Engine (Spark Ig.)	No	Gas	8	(3-38)	0.084	4.0
	Gas Turbine						
7.	Turbojet	---	Oil	5	(3-39)	0.002-0.006	0.11-0.32
8.	Turbojet	---	Gas	46	(b)	(0.004)(b)	(0.2)(b)

(a) Figures in parentheses estimated assuming supercharging doubles NO_x emissions (based on lines 3 and 4).

(b) Estimated assuming gas will give same amount of NO_x as turbo fuel. This may be open to question and probably penalizes the turbojet engine. If the turbine engine responded to gas fuel in the same way as the diesel engine, the NO_x emissions would be of the order of only 0.04 lbs/million BTU.

Gas turbine engines in stationary applications in the U.S. are estimated to have a total current capacity of 51 million HP (assuming 60% of the worldwide stationary turbine population is in the U.S.). The bulk of these engines (say, 90%) are fueled with natural gas.

3.1.3.2 Other Combustion Processes

Major amounts of the total fuels burned and NO_x emissions released in the United States are associated with small-scale combustion processes. These include important non-industrial uses in domestic and commercial heating and hot water supply, and a wide variety of incinerators or burning for the disposal of solid wastes. This is much the largest stationary use of fuels, larger than the electric utilities, but it is a less severe type of combustion. Its contribution to NO_x is significant, particularly in residential areas.

"Commercial" in this discussion denotes multiple-unit heating and small appliances used in business, which are similar to household equipment and appliances such as space and water heaters, ranges and clothes dryers.

Some 30% of the total fossil fuels used in the U.S. for energy production (transportation excluded) is consumed in domestic and commercial heating (3-40). This represents 12,432 x 10^{12} BTU's annual consumption, and it substantially exceeds the 9,994 x 10^{12} Btu's required for power generation by the electric utilities.

Limited statistics for the breakdown into fuel types within this sector show the following division for the 29 million domestic, automatic central-heating units in use in 1967: (3-41)

Gas Burners	18,184,321
Oil Burners	10,692,825
Coal Stokers	263,964
Total	29,141,110

For space heating and cooking only, the following quantities are shown by fuel type and equivalent Btu content, for 1966: (3-42)

	Natural Gas 10^9 ft^3	Distillate Fuel Oil 1000 Bbls.	Residual Fuel Oil 1000 Bbls.
Quantity	5,761	472,778	167,471
Equivalent BTU x 10^{12} (3-43)	5,945	2,832	1,052

The use of gas for domestic heating purposes only in the U.S. was estimated as follows, as of January 1968: (3-44)

Number of Customers-10^6	Type of Use	Heat Use Avg. Btu/Unit/Yr-10^5	Total Heat Use Btu-10^{12}
28.8	Heating Units (1 & 2 Family)	1,020	2,938
33.0	Hot Water	300	990
38.2	Ranges	110	420
		Total	4,348

These statistics all show the extremely large number of NO_x emitters involved in the domestic and commercial heating categories, and the substantial quantities of fuel used.

The rate at which fuel is used for domestic water heaters, ranges, gas refrigerators, clothes driers, etc. remains reasonably constant throughout the year, but the much larger amount required for space heating is consumed during the six-month winter period. Thus, the rate of domestic fuel consumption during the winter greatly exceeds that indicated by the 30% of total annual fuel use shown above, and in mid-winter months in many areas it can be well over 50% of all fossil fuels consumed.

In addition to this very large rate of fuel use during the heating season, the products of domestic combustion are vented close to ground level. Under adverse conditions such as stagnation or aerodynamic downwash, particularly in densely populated areas, these fumes will become an immediate part of the ambient atmosphere. The extent of this pollution is not visually as evident with clean burning gas and oil fuels as chimney soot was in the past, when coal was the main fuel, but the NO_x formed and other less visible combustion products are still present.

The contribution of residential space heating to NO_x is suggested by data on seasonal and diurnal effects in fuel usage for space heating from CAMP and other sources, which indicate that the variations in SO_2 emissions in urban areas may be correlated with changes in residential heating throughout the day and throughout the year (3-45, 46, 47). This confirms the conclusions drawn from preliminary data in an earlier study of the area near Menlo Park, California (3-7). The NO_x concentration was higher during the winter and closely followed natural gas consumption in the area. Easily detectable concentrations were present during periods of very low wind velocity. The highest concentrations were 0.53 ppm NO and 0.15 ppm NO_2. The NO greatly exceeded NO_2 during the early morning hours and during the late afternoon and evening. During mid-day the NO and NO_x dropped, while NO_2 increased and was somewhat higher than NO.

The relatively poor dispersion of domestic chimney gases pointed out in these studies means that a given amount of NO_x at ground level will have a greatly aggravated effect on ambient air compared to the same amount emitted from a tall utility stack. The thickness of the air layer into which the combustion gases are distributed will be much less for ground-level sources and under adverse conditions this effect may be significant. Commercial buildings and apartments will presumably show an intermediate effect.

The effect of unit size and severity of operation reported by Mills, et al., from Los Angeles data has a direct bearing on NO_x emissions from domestic heating units (see Section 3.2). According to their correlation (Figure 3-13), a typical gas-fired domestic furnace of 150,000 BTU/hr capacity produces NO_x at about 12% of that produced in a large utility boiler of 10^{10} BTU/hr, for a given amount of fuel. A similar ratio appears for oil-fired equipment. This means that while domestic and commercial heating units consume some 125% of the fuel used in utility boilers, their total contribution to NO_x in the U.S. will be only 12% of this ratio, or about 7% of all NO_x in the U.S. compared to 22% for the utilities.

3.1.3.3 Incineration and Other Burning

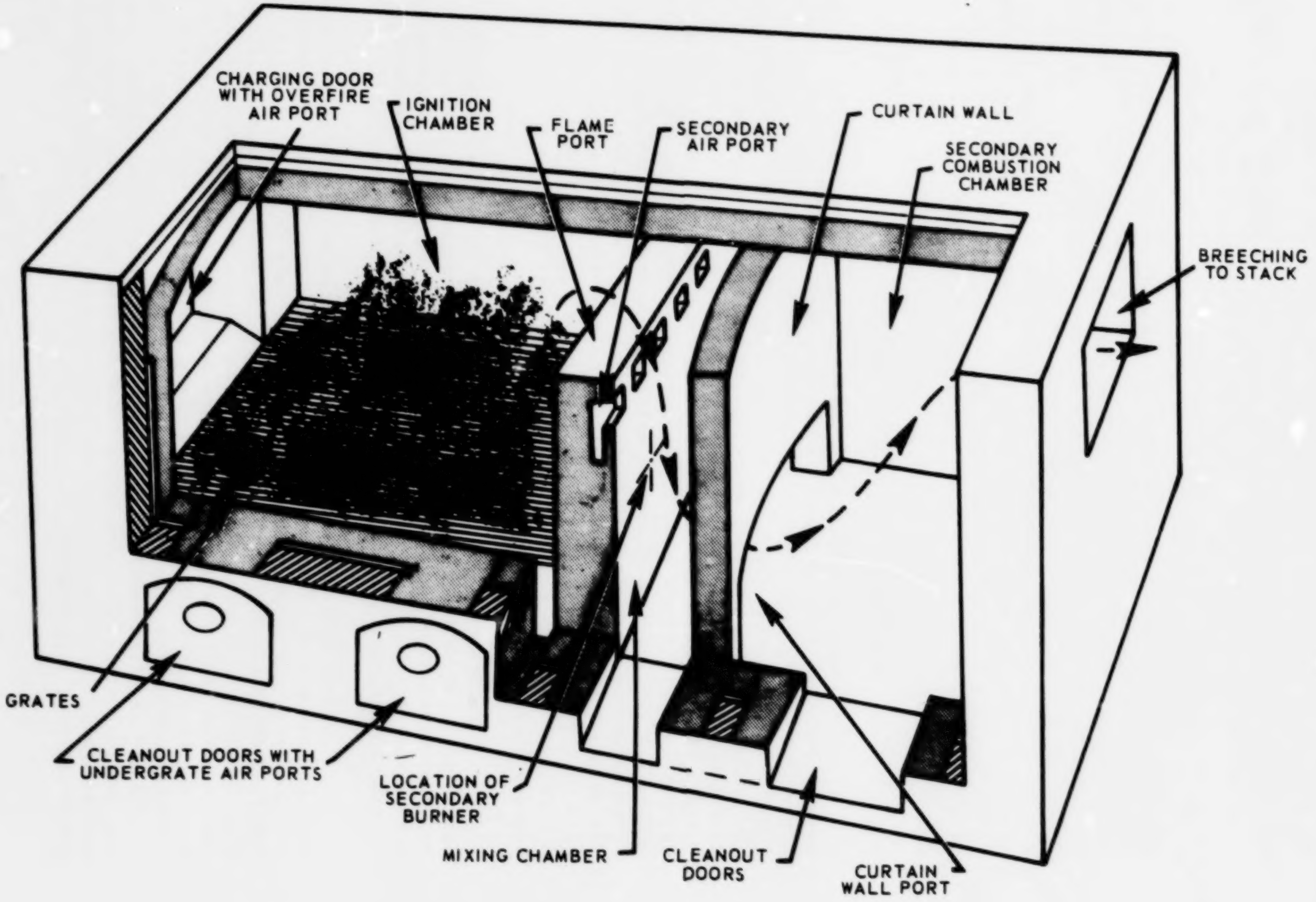
Preliminary results of a survey conducted by the Public Health Service indicate that household, commercial and industrial solid waste production in the U.S. is about 10 pounds per capita per day, or 360 millions tons per year. About 190 million tons per year (or 5.3 pounds per day per capita) is collected for disposal and the remainder is either disposed of on site or handled by the household or establishment itself (3-48). An estimated 177 million tons of this material is burned in the open or in incinerators (3-49). An additional 550 million tons of agricultural waste, 1.1 billion tons of animal wastes are generated each year (3-48). It is estimated that one-half of the agricultural wastes are burned in the open and that except for 48 million tons of coal refuse consumed by fire each year, no animal or mineral wastes are burned (3-49). The quantity of material consumed by structural fires is estimated to total about 8 million tons a year (3-49).

Incineration and open burning are used to reduce the weight and volume of solid waste. High temperature incineration with excess air reduces emissions of particulates, carbon monoxide, and smog forming compounds such as aldehydes, hydrocarbons, and organic acids which are typical in open burning, but tends to increase nitrogen oxides emissions.

Figure 3-5 shows a typical multiple-chamber incinerator. Combustion products are formed by contact between underfire air and waste on the grates in the primary chamber. Additional air (overfire air) is admitted above the burning waste to promote gas phase combustion. Gases from the primary chamber flow to a small mixing chamber where more air is admitted and then to a larger secondary chamber where more complete oxidation occurs. Auxillary burners are often installed in this chamber to increase combustion temperature to 1400°F to 1800°F. A total of 150 percent excess air is often supplied to promote oxidation of combustibles. Sizes and configurations of incinerators vary with the service for which they are designed. References (3-4) and (3-50)contain information on design parameters for incinerators.

Figure 3-5

Cutaway of an in-line
Multiple-Chamber Incinerator


CHARGING DOOR WITH OVERFIRE AIR PORT
IGNITION CHAMBER
FLAME PORT
SECONDARY AIR PORT
CURTAIN WALL
SECONDARY COMBUSTION CHAMBER
BREECHING TO STACK
GRATES
CLEANOUT DOORS WITH UNDERGRATE AIR PORTS
LOCATION OF SECONDARY BURNER
MIXING CHAMBER
CLEANOUT DOORS
CURTAIN WALL PORT

NO_x emissions from incineration and other burning are estimated as shown in Table 3-10:

Table 3-10

Estimated National Emissions from Incineration and Other Burning - 1968 (3-49)

	Quantity 10^6 Tons/Yr	NO_x Emission 10^3 Tons/Yr
On-Site Incineration	57	71
Municipal Incineration	16	16
Conical Burner Incineration	27	9
Open Burning	77	420
Agricultural Burning	275	275
Total	452	791

NO_x levels in incinerator flue gases are in the range of 50-80 ppm (3-51), and 8-130 ppm in gas from open burning, where the NO_x level varies with cycle time (3-52). The volumes of various solid wastes consumed in each disposition and the emission factors are difficult to measure, particularly for open burning. The factor for open burning appears high relative to factors for incineration, since it does not seem reasonable that open burning, in which radiation to the sky cools the flame, would produce more NO_x than combustion in a closed system. It is reasonable to assume that these estimates are grossly overestimated, because of the lack of validity of available factors. Consequently, more conservative estimates of NO_x emissions from refuse burning have been utilized to develop emission inventories and projections for the U.S. in Tables 3-22 through 3-29.

The emission factor for open burning given in the literature serves as an excellent example of the uncertainties involved. Reported values vary from 0.6 (3-53) to 11 (3-10) pounds of NO_x per ton of waste burned, with both values given at times in the same report. The value of 0.6 was quoted originally as an average for the burning of paper, garden trash or combined refuse. The value of 11 was an interpretation of data obtained from simulated open burning (3-52). A few grab samples were obtained at various times during a cycle in which burning rate, temperature, and gas composition fluctuated over a wide scale. The NO_x concentration, as parts per million, were very low: 2 to 130. The value of 11 may be chosen as an emission factor for open burning as a reasonably safe maximum, but it is clear that new data are required, preferably with a continuous measuring system, to get a factor on which any confidence can be placed. The conversion of these concentrations to pounds per ton of refuse is highly questionable and no basis is given in reference (3-52).

3.1.3.4 Metallurgical Processes

- The Blast Furnace

The blast furnace is the central unit in which iron ore is reduced, in the presence of coke and limestone, for the production of pig iron. The blast furnace itself is normally a closed unit and therefore has no atmospheric emission. A preheated air blast is supplied to the furnace from the blast furnace stove, through nozzle-like openings called tuyeres. The subsequent reactions in the blast furnace are not pertinent to this discussion. However, excellent descriptions are available, such as the complete discussion from ore to finished steel published by United States Steel Corporation (3-54).

The hot blast reacts with the coke to produce heat and carbon monoxide. The excess carbon monoxide (beyond that needed in reducing the ore) which leaves the top of the blast furnace along with other gaseous products and particulates is known as blast furnace gas. This gas is cleaned up to remove the particulates, which could later cause plugging, and is available for heating purposes. It contains about 1% of hydrogen and 27% carbon monoxide, and has a heating value of approximately 92 Btu/ft^3. (3-54)

Four to five tons of blast furnace gas is generated for each ton of pig iron produced. Some 18 to 24% of this gas is used as fuel to heat the three blast furnace stoves which are usually associated with each blast furnace. Two are generally on heat while the third is on blast.

The blast furnace stove is a structure some 26 to 28 feet in diameter and about 120 feet high. A roughly cylindrical combustion chamber extends to the top of the structure and the hot combustion gases pass through a brick checkerwork by reverse flow to the bottom and thence to the stack. The checkerwork usually contains 275,000 ft^2 of heating surface and has about an 85% thermal efficiency. Unlike the conventional regenerators, which extract heat from the waste combustion gases, the blast furnace stove is heated by burning fuel. The stored heat is then used to preheat air for the combustion of fuel in the furnace to be served.

The low calorific value of blast furnace gas would indicate that due to dilution and low flame temperature the NOx content of the combustion gas from blast furnace stoves should be low. This is confirmed by unpublished data on stack gas samples ranging from 1.7 to 6.6 ppm NO_x for an average of 3.6 ppm. However, the NO_x emission, based on the Btu output is estimated at 26 lb. NO_x/hr.

or 114 tons/yr. for a typical blast furnace*. On June 1, 1968 there were 173 furnaces on blast in the U.S. (3-23), which indicates an annual atmospheric burden of 20,000 tons of NO_x from blast furnace operations. This is 0.7% of the estimated 1965 industrial NO_x emission (3-56) in the U.S.

- The Open Hearth Furnace

Steel making by the open hearth process has been decreasing since it reached a peak in 1956, when it constituted 90% (103 million tons) of the total production. In 1967 production had declined to 55% and by 1972 only 25 million tons may be so produced. Phase-out is expected between 1980 and 1990. (3-23) Regardless of this dramatic decline in the use of open hearth processes, due to the inroad of pneumatic steelmaking processes, its NO_x emission potential deserves consideration.

The open hearth furnace is both reverberatory and regenerative, similar to the glass melting furnaces. It is reverberatory in that the charge is melted in a shallow hearth by heat from a flame passing over the charge and by radiation from the heated dome. It is regenerative in that the remaining heat in the partially spent combustion gases, from the reverberatory chamber, is accumulated in a brick filled chamber (checkers) and released to preheat the incoming combustion air when the cycle is reversed. Fuel of low calorific value such as B.F.G. may be preheated by the checkers as well as the combustion air, in order to obtain the high temperatures required.

Hot metal from the blast furnace, pig iron, scrap and lime are the usual materials charged to an open hearth furnace. These are heated over a period averaging 10 hours, at a temperature as high as the refractories will permit. Fuel oil is the preferred fuel and is burned with excess air to provide an oxidizing influence on the charge. These conditions favor NO_x formation, and an analysis of 10 open hearth stack samples shows a range of 22.9 to 671 ppm for an average of 243. In another set of tests, an average of 320 ppm was obtained. These analyses were taken while an oxygen lance was being used to enhance the steel producing reactions.

It is estimated that 490 lbs of NO_x are emitted in the production of a 200 ton batch of steel. These calculations are based on 3.2 million BTU of fuel/ton of steel (3-54) and 0.76 lbs NO_x/million Btu. If the U.S. production of steel in 1967 was 127,213,000 tons (3-23) and 55% was produced in open hearth furnaces, then roughly 85,000 tons of NO_x were emitted to the atmosphere. This represents 3.1% of the estimated 1965 industrial NO_x emission in the U.S. (3-56).

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* This calculation is based on a gravity of 1.02 for Blast Furnace Gas (B.F.G.) (3-54), which equals 0.08233 lbs/ft^3. If a medium value of 4.5 tons of B.F.G. produced/ton of pig is assumed then 109,300 ft^3 of B.F.G. is produced/ton of pig, or 7,150,000 ft^3 for 65.4 tons (3-55) which is the average production/blast furnace/hour. If a medium value of 21% of the B.F.G. having a Btu content of 90 is used to heat the stoves, then 135,180,000 Btu/hr. are used or 67,590,000 for each of the two stoves on heat. This translates (3-9) to 13 lbs NO_x/hr. or 26 lbs/hr. for the two stoves, or 114 tons/yr.

- Coking Ovens

Coke is an essential component in the making of pig iron and steel; the coke ovens are generally an integral part of the steel plant complex. In 1967, coke ovens in the U.S. produced 63,775,000 tons of coke. One sixth (92 million tons) of the total bituminous coal produced was charged to coke ovens. On the average, 1.43 tons of coal was required for each ton of coke produced. (3-23)

Commercial coke ovens are built in batteries consisting of 40 to 70 slot-type coking chambers arranged side by side. The usual chamber is about 14 ft high, 40 ft long and 18 inches in width. The side walls or liners are built of silica brick, and the space between the chambers constitutes flues in which fuel gas burns to supply the required heat. Each lb. of coal carbonized requires 1000 to 1150 Btu, and flue temperatures are as high as 2700°F. (3-57) The remaining heat in the partially spent combustion gases is accumulated in a brick checkerwork, which releases it to preheat the combustion air when the cycle is reversed. This is a typical regenerative cycle, to conserve fuel and gives a higher flame temperature.

The coal in the coking chambers undergoes destructive distillation during a heating period of about 18 hours. The noncondensable gaseous product is known as coke oven gas and on a dry basis has a heating value of about 570 Btu/ft^3. Approximately 35% of the coke oven gas produced is used in heating the oven.

The trend in new coke oven construction is toward higher ovens (16.5 to 19 ft. vs. the usual 13-14 ft), which will increase coal throughput by 75%. (3-58) This increase is due in part to higher temperatures permitted by improved refractories and more uniform heating designs. This trend will tend to increase NO_x emission.

Actual analysis of two coke oven stack gas samples gave values of 41 to 50 ppm NO_x or an average of 45 ppm. In another test, an average of 28 ppm was obtained.

It is roughly estimated that in the carbonization of 92 million tons of coal in the U.S. during 1967, about 6,000 tons of NO_x were emitted.* This represents 0.23% of the estimated 1965 industrial NO_x emission in the U.S. (3-56)

* These calculations are based on a slot oven holding 20 tons of coal and provided with 30 separate heating flue combustion chambers. A heating period of 18 hrs. is assumed and a value of 1,100 Btu required to carbonize one pound of coal. This calculates to 81,000 Btu/flue/hr. When gas is burned at this rate, 0.005 lbs of NO_x are produced per hour. (3-9) For 30 flues over 18 hrs., 2.7 lbs of NO_x is produced, which is the amount produced in the carbonization of 20 tons of coal. For 92 x 10^6 tons, the NO_x production equals 6,120 tons.

The cupola furnace is similar in many respects to the blast furnace. Its function is to melt scrap and pig iron for subsequent processing in steel production. Like the blast furnace, its off-gas contains usable quantities of carbon monoxide which could be recovered and burned to preheat the air blast. (3-59)

The reducing conditions that tend to exist in the cupola furnace would not be expected to produce the quantity of NO_x that the high temperatures would suggest. Available data indicate a concentration of 13 ppm. NO_x in the vent gases or 0.11 lbs/ton of metal produced. (3-54) A questionnaire survey of 1680 U.S. foundries by NAPCA and the Department of Commerce shows that 14,600,000 tons of iron castings shipments were produced by cupolas in 1966. On this basis, iron cupolas emitted 805 tons of NO_x to the atmosphere during that year.

- The Basic Oxygen Furnace (BOF)

The use of air for bottom blowing in the refining process for steel production has been common practice since 1870 but in recent years it has declined to minor importance. The use of pure oxygen for top blowing has increased rapidly and this is now a major refining method. Bottom blowing was characteristic of the Bessemer process which is no longer used, whereas the basic oxygen process (BOF) is the more common use of top blowing. Since neither of these processes is, in itself, a producer of NO_x, the reader is referred to the literature for process description. (3-54)

The BOF method produces substantial amounts of carbon-monoxide and if this is permitted to burn off, some NO_x is produced by reaction of the hot gas with air outside the furnace. This can be avoided by use of a suitable hood system to collect the gas for other uses. (3-60)

Other Furnaces using either regenerative or recuperative preheat of the combustion air are used, in addition to the open hearth, coke ovens and blast stoves, for such lesser applications as reheating and soaking pit furnaces. Actual analysis of soaking pit stack gases have given average NO_x values of 25.8 and 21.5 ppm. These values are in line with coke oven emissions (45.6 and 28.3) but considerably lower than open hearth values (243 and 320). NO_x emissions from soaking pits stack gases are estimated at 550 tons/year in the U.S., based on 0.086 lbs. NO_x/ton of ingot steel production, (3-55) and ingot steel production of 127 million tons/year in the U.S.

Another NO_x emission source, differing somewhat from the conventional furnace, is sintering operations. In this instance, finely divided iron-bearing material is mixed with a fuel, such as coke breeze, to give a product suitable for blast furnace use. The mixture is spread on a traveling grate and ignited by gas burners. The burning is continued by air drawn down through the grate. Analysis of stack gases from such sintering produces NO_x values of 47.2 to 36.3 ppm. NO_x emissions from sintering stack gases are estimated at 27,000 tons/year in the U.S., based on 1.04 lb. NO_x/ton of sinter and sinter production of 51 million tons/year in the U.S. (3-55)

3.1.3.5 Kilns - Cement, Limestone and Ceramics

The kiln-type furnace is used in the production of cement clinker, quicklime and the firing of ceramic-type products. The rotary kiln predominates the cement industry and is also extensively used for limestone calcining. However, the latter industry uses, to a considerable extent, the vertical shaft kiln both in its original form, which is gradually being retired, and the newer high-capacity design. For ceramic firing, the tunnel kiln is used for the smaller, more fragile items and the beehive kiln for larger items such as drainage pipe.

Cement clinker is produced by sintering intimately ground mixtures of limestone with suitable clays, shales, or marls. Such mixtures, either as dry feed or wet slurry, are gradually heated to sintering temperature (up to 2900°F) (3-61) in rotary-type kilns. The product is a clinker which, when finely ground and mixed with a small amount of gypsum to control set, is the portland cement of commerce.

A rotary kiln is essentially a steel cylinder, varying in diameter from 8 to 16 feet and 150 to 500 feet long, lined with a refractory material. These kilns are slightly inclined and rotated at about 1 rpm. Raw feed entering at the high end works its way gradually down to the lower end over a period of 2 to 4 hours. Preheated air and fuel are fired at the lower end, so the combustion gases travel countercurrent to the feed. During its slow travel down to the hot end of the kiln, a series of reactions take place ending in a partial melting. This sintered material is the cement clinker referred to above. The hot clinker is cooled by incoming combustion air which improves the overall thermal efficiency and gives a higher peak temperature.

The capacity of individual kilns has been increased in recent years to more than 10,000 bbl/day (376 lbs/bbl), but 2,000 to 6,000 bbl/day is representative of the industry.

In the U.S. in 1967, some 188 plants produced about 369 x 10^6 barrels of cement. The fuel consumed was as follows: (3-23)

	Fuel Consumed in Cement Industry During 1967		
	Coal 10^3 Short Tons	Oil 10^3 Bbls (42 Gal)	Natural Gas 10^6 Ft^3
	9,096	4,956	159,717
Equivalent Btu's - 10^{12}	236	30	196

Average fuel consumption in 1967 was 1.25 x 10^6 Btu/barrel or 6.66 x 10^6 Btu/ton of cement.

Limestone rock occurs in two principal variations. If it is almost entirely calcium carbonate ($CaCO_3$), it is known as a high calcium limestone. If a considerable portion of the calcium carbonate content is displaced with magnesium carbonate (from 30 to 45%), it is known as a dolomitic limestone. Either of these limestones, when heated, can lose carbon dioxide (CO_2) to give either the quicklime or the dead-burned lime of commerce.

At calcination temperatures of 1700-2450°F, dissociation of the limestone proceeds gradually inward from the outer surface of the stone particle. Temperatures in the higher range are required for dissociation to reach the center of the particle. Since a gradual temperature increase is preferred, the rotary kiln is particularly suited to limestone calcination. Product heat is recovered as preheat for the combustion air, as in cement kilns.

Excessive heat is avoided if a high quality or active quicklime is desired. Longer heating at sintering temperature is required to produce dead-burned dolomitic lime for refractory furnace linings.

Vertical kilns were first used for limestone calcination, but these have been largely replaced with rotary kilns. However, a few new installations of vertical kilns of improved design have been announced. (3-62) The capacity limit, which was a major disadvantage, has been extended up to 500 tons/day, which is the equivalent of modern rotary kilns.

Vertical kilns are more thermal efficient than rotary kilns. Typical fuel consumptions are 5×10^6 Btu/ton (3-62) for vertical kilns and 7×10^6 for rotary.

The 1967 U.S. production of lime was 17,974,000 short tons in a total of 209 plants. Of this amount, 33 plants produced 63% of the total. (3-23) Since fuel consumption statistics are not available for manufacturing lime, a value of 6×10^6 Btu/ton was used to estimate the thermal requirements for limestone calcination in the U.S. in 1967 at 108×10^{12} Btu. No reliable breakdown as to the use of coal, oil or gas appears to be available, but the literature suggests that a gradual switch to gas is in progress.

The ceramics industry embraces a multitude of products which include the more general headings of refractories, vitreous enamels, whitewares, abrasives, structural clay products and ceramic mineral preparation. The larger kilns used by the industry are of two types: tunnel and beehive.

The tunnel kiln varies from 2 to 10 ft. wide and 4 to 8 ft. high by 75 to 100 ft. long. These kilns are gas or oil fired, with the burners placed near the center of the tunnel. The material being fired moves slowly into the hot zone and is then cooled slowly in the remaining length of travel. Combustion air is introduced at the exit end and is preheated as it passes over the hotware leaving the kiln.

The "beehive" kilns are shaped as the name indicates and vary in size up to 60 ft. in diameter. Burners are spaced around the periphery and the combustion gases are diverted towards the dome, then down through the ceramic material stacked on the floor. Ducts under the floor lead the gases to a common stack which usually serves four kilns.

Particulates are the major pollutants associated with cement, lime, and ceramic kiln operations. Limited data are reported in the literature on NO_x emissions from tunnel and beehive ceramic kilns, but no data have been found on NO_x from cement or lime kilns. Since large volumes of fuel are consumed and combustion air is preheated, significant NO_x formation would be anticipated in cement and lime kiln operations.

Estimated NO_x emissions from kiln operations in the U.S. during 1967 are given in Table 3-11.

TABLE 3-11

ESTIMATED NO_x PRODUCTION FROM KILNS - U.S., 1967

	Tons/Yr	% of Total Emissions
Cement Kilns	108,000	0.8
Lime Kilns	21,000	0.15
Ceramic Kilns	21,000	0.15
Total	150,000	1.1

Estimated emissions from single large kilns are shown below in Table 3-12.

TABLE 3-12

ESTIMATED NO_x FROM SINGLE LARGE KILNS

	Cement	Lime	
	Rotary	Rotary	Vertical
Product Capacity	10,000 B/D (1,880 T/D)	500 T/D	500 T/D
Firing Rate, MM Btu/Hr	416	147	105
NO_x-lb./Hr			
Gas Fired	120	35	24
Oil Fired	270	80	53
Coal Fired	290	86	57
NO_x, ppm in Flue Gas*			
Gas Fired	190	160	150
Oil Fired	390	210	290
Coal Fired	400	320	300

* Assuming no dilution between kiln and stack.

Cement and lime kiln emission estimates are based on the fuel consumptions discussed in this section and the correlation between NO_x production rate and heat input to the combustion unit (3-9) shown in Figure 3-13.

There is limited NO_x emission data for tunnel kilns used for firing ceramic items such as pottery. The results of five tests varied from 3 to 66 ppm with an average of 24 ppm. (3-9) Gas firing was used in all instances.

A large beehive kiln which can accommodate 1000 tons of ceramic ware requires a heat input of up to 15 x 10^6 Btu/hr. (3-9) Such a kiln, based on similar emission factors to those used above, will produce 2.2 lbs of NO_x/hr if gas fired and 4.8 if oil fired. If four kilns are served by a single stack, as is usually the case, the stack emission will be 8.8 lbs of NO_x/hr for gas and 19 for oil.

As recommended by Smith (3-65), emissions for coal for this table were assumed to be slightly higher than the correlation for oil. For cement kilns, combustion air was assumed to be preheated to 500°F, as reported for lime kilns (3-64). The preheat was reflected by basing NO_x emissions on a heat input 1.1 times the firing rate.

3.1.3.6 Glass Manufacture

The raw materials used in glass manufacture consist primarily of silica sand, soda ash, limestone and cullet (crushed waste glass). In the production, e.g., of window and plate glass, temperatures in the range of 2750 to 2850°F are required to melt these raw materials into a viscous liquid.

The furnaces used are of the pot type, when only a few tons of a specialty glass is involved, or the continuous tank type for larger quantities. By far the larger amount of glass is melted in the tank furnaces, and only these will be considered in connection with NO_x control.

The continuous tank furnaces have a holding capacity of up to 1400 tons and a daily output of as much as 300 tons. Figure 3-6 is a cutaway view of a side port regenerative glass-melting furnace (3-4). The "batch" feed is introduced at the left or "melting end" which, at least for the harder varieties, is maintained at as high a temperature as the structural materials will permit. The glass receives its heat through its surface by radiation directly from the flames and the almost white-hot crown. As the mass fuses, it passes into the "fining zone" and finally through the submerged throat of the bridgewall into the "working zone."

The combustion gases, on leaving the melting zone, retain a considerable amount of heat. This is reclaimed in a regenerator or brick checker chamber. When the cycle is reversed, combustion air is preheated by passing through the brick work. Preheating increases the flame temperature.

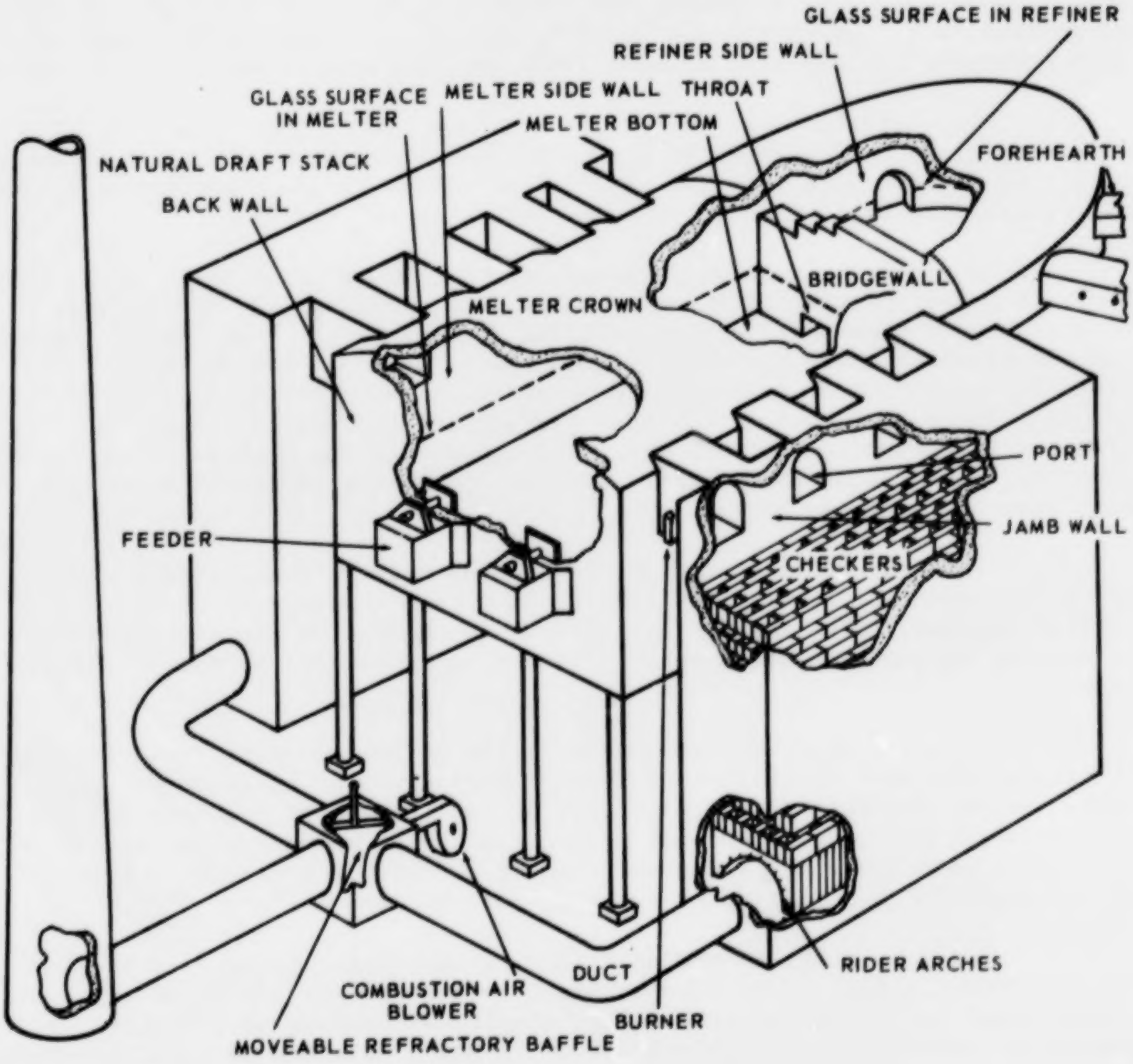
A variation of the side-port firing is the end-port fired furnace. It is possible that the different type of firing could influence NO_x emission. In the end-port furnace a single burner instead of multiple burners is located at one side of the end of the tank. The combustion gases follow a U-shaped path and enter a checker chamber for heat reclamation. Reversal of the cycle is then similar to the side-port firing.

Coal, as such, is not used in glass melting. It is used in the form of producer gas, or in a power plant to produce electrical energy. Since molten glass is conductive, the use of electrical heating as a booster, to supplement fuel firing, is gaining favor (3-66). Gas, and to a lesser extent, fuel oil are the preferred fuels.

The flue gas from glass-melting tanks is the major source of NO_x emissions in the glass industry. The operation of these tanks is similar to the open hearth furnaces used in steelmaking, using regenerative checkerwork sets to absorb heat from the combustion gases for subsequent release to the incoming combustion air. This is accomplished by a reversing valve which puts each checkerwork set through its heating and cooling cycles, in turn. The

FIGURE 3-6

REGENERATIVE SIDE PORT GLASS-MELTING FURNACE


GLASS SURFACE IN REFINER
REFINER SIDE WALL
GLASS SURFACE IN MELTER
MELTER SIDE WALL
THROAT
MELTER BOTTOM
NATURAL DRAFT STACK
FOREHEARTH
BACK WALL
BRIDGEWALL
MELTER CROWN
PORT
FEEDER
JAMB WALL
CHECKERS
RIDER ARCHES
DUCT
COMBUSTION AIR BLOWER
BURNER
MOVEABLE REFRACTORY BAFFLE

sequence of intense high temperature combustion and with combustion air preheat quenching in the checker-work raises NO_x emission to levels perhaps 5-fold those experienced in a steam boiler of equivalent heat release. This observation is based on measured emissions of 0.87 pounds NO_x/million Btu fired for glass melting tanks firing an average of 38 million Btu of gas per hour (3-9), compared to 0.13 pounds NO_x per million Btu of heat input for gas firing in normal combustion equipment of this size (see Figure 3-13).

Normal combustion supplies the lesser amounts of heat used in glass annealing and tempering, and these are only minor sources of NO_x.

Annual NO_x emissions from the U.S. glass industry are roughly estimated at 110,000 tons for 1967, or about 1.3% of total NO_x pollutants. This is based on reported fuel usage in 1962 (3-67), and reported glass production for 1962 and 1967. (3-68) A 300 T/D glass melter, currently the largest size, will consume about 92$\overline{M}$ Btu/hr of fuel and discharge an estimated 80#/hr of NO_x, based on an emission factor of 0.87#/$\overline{M}$ Btu of fuel fired. This factor is taken from a set of tests run in Los Angeles where the NO_x concentrations in glass-melter stack gas ranged from 435 to 1320 ppm, averaging 570 ppm. (3-9)

The type of furnace and firing as shown in Figure 3-6 is similar to those used in producing steel by the open-hearth furnace. Actual chemical analysis of the stack gas from an open-hearth furnace when fired with 70% gas and 30% oil varied from 500 to 800 ppm of NO_x with an average of 700 ppm. Similar results were found for four glass furnaces. The values ranged from 435 to 1320 ppm with an average of 570 ppm. (3-9) Other data from analysis of exhaust gases from a large regenerative, gas-fired furnace melting amber glass were 137 ppm whereas a value of 725 ppm was obtained when melting flint glass. (3-4)

3.1.4 Manufacture and Uses of Nitric Acid

3.1.4.1 Nitric Acid Manufacture

All nitric acid manufactured in the United States is made by the catalytic oxidation of ammonia. Air and ammonia are preheated, mixed, and passed over a catalyst, usually platinum-rhodium. The following reaction occurs:

$$4NH_3 + 5O_2 \longrightarrow 4NO + 6H_2O \qquad (3\text{-}1)$$

The stream is cooled to 100°F or less, and the NO reacts with more oxygen to form nitrogen dioxide and its liquid dimer, nitrogen tetroxide.

$$2NO + O_2 \longrightarrow 2NO_2 \rightleftharpoons N_2O_4 \qquad (3\text{-}2)$$

NO_2 is a reddish-brown gas with a sharp odor. The liquid and gas then enter an absorber tower. Added air is directed to the bottom of the tower and water to the top. The NO_2 (or N_2O_4) reacts with water to form nitric acid and NO, as follows:

$$3NO_2 + H_2O \longrightarrow 2HNO_3 + NO \qquad (3\text{-}3)$$

The formation of one mole of NO for each 2 moles of HNO_3 makes it necessary to reoxidize NO after each absorption stage, as the gas rises up the absorber and limits the level of recovery that can be economically achieved.

Acid product is withdrawn from the bottom of the tower in concentrations of 55% to 65%. The air entering the bottom of the tower serves to strip NO_2 from the product and supply oxygen for reoxidizing the NO formed in making nitric acid (equation 3).

Normally, high pressures of 80-120 psi are employed in the oxidation and absorption operations. Tail gas from the absorber passes through an entrainment eliminator for removal of nitric acid mist. Tail gas is then reheated by exchange with the gases from ammonia oxidation and is directed to a turboexpander for energy recovery.

Before corrosion resistant materials were developed, the ammonia oxidation and absorber operations were carried out at essentially atmospheric pressure. Because of the low absorption and NO oxidation rates, much more absorption volume was required, and several large towers were placed in series. Some of these low-pressure units are still in operation, but they represent less than 5% of the current U.S. nitric acid capacity (3-69). Improved technology has made the "pressure process" more economical, and it is the preferred process in the United States. Over 90% of the U.S. nitric acid plant capacity is believed to be of the pressure type (3-69). A typical flow plan is shown in Figure 3-7. Except for leaks, the only source of NO_x emissions is the tail gas from the unit.

Combination pressure plants carry out the ammonia oxidation step at low pressure and absorption at high pressure. Intermediate pressure plants carry out both operations at intermediate pressures.

For most uses, the 55-65% nitric acid made by ammonia oxidation is satisfactory. However, for some uses, high strength acid is required. These requirements are met by concentrating the lower strength acids.

Figure 3-8 illustrates a nitric acid concentration unit using extractive distillation with sulfuric acid. A mixture of strong sulfuric acid and 55-65% nitric acid is introduced at the top of a packed column, and flows down the column countercurrent to the ascending vapors. Nitric acid leaves the top as a 98% nitric acid vapor containing small amounts of NO_x and oxygen, resulting from dissociation of nitric acid. The vapors pass to a bleacher and a condenser to condense nitric acid and separate NO_x and oxygen, which pass to an absorber column for conversion to, and recovery of, nitric acid. Air is admitted to the bottom of the absorber. Dilute sulfuric acid is withdrawn from the bottom of the tower and is sent to sulfuric acid concentration or used for other purposes. The system usually operates at essentially atmospheric pressure.

Absorber tail gas is the principle source of NO_x emissions from nitric acid manufacturing. Minor sources are nitric acid concentration, and filling of storage tanks and shipping containers.

Nitrogen oxide emissions from nitric acid manufacturing are estimated at 145,000 tons/yr for 1967, about 1% of the NO_x from all pollution sources or 2% of the pollution from stationary sources. This figure is based on 6.12 million tons of nitric acid production in 1967 (3-70) and an average emission factor of 45 lb. NO_x/ton of acid (3-69). Without controls, an 800 T/D plant (the largest currently built) would emit about 1500 lb/hr of NO_x. Typical tail gas contains about 0.3 vol% (3000 ppm) of NO_x with about equal concentrations of NO and NO_2 (3-69). Tail gas is typically reddish-brown or yellow.

For any nitric acid plant, NO_x content of the tail gas is affected by several variables. High levels may be caused by insufficient air supply, high temperatures in the absorber tower, low pressure, producing acid at strengths above design, and internal leaks which permit gas from ammonia oxidation with high nitrogen oxides content to enter the tail gas streams. Careful control and good maintenance are required to hold tail gas nitrogen oxides content to a minimum.

FIGURE 3-7

FLOW DIAGRAM OF A TYPICAL 120-TON-PER-DAY NITRIC ACID PLANT UTILIZING THE PRESSURE PROCESS

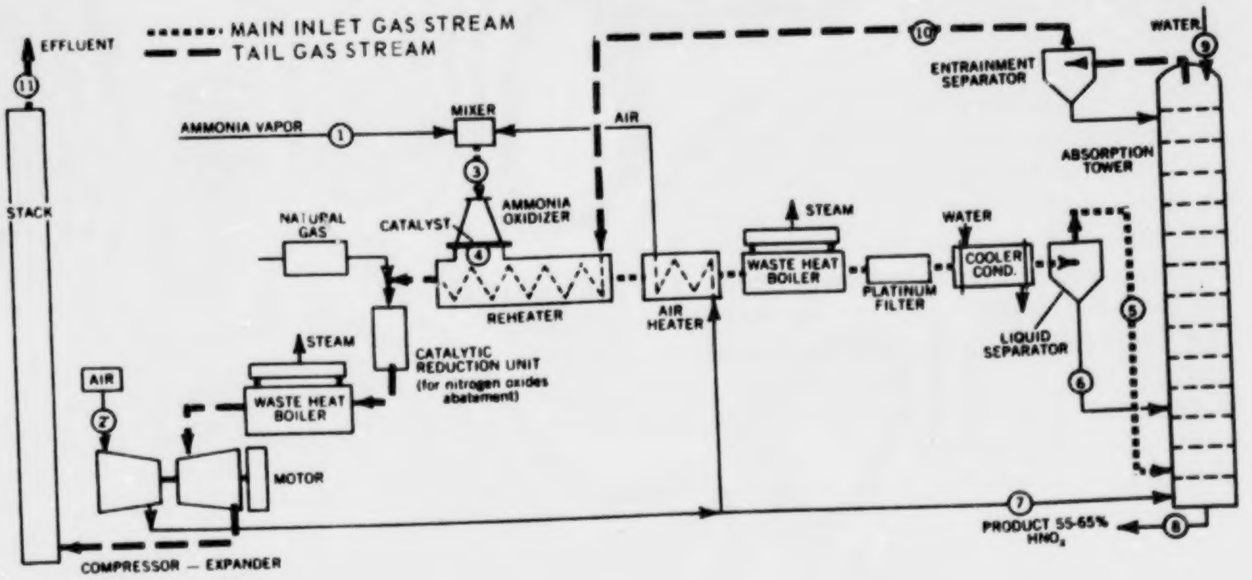
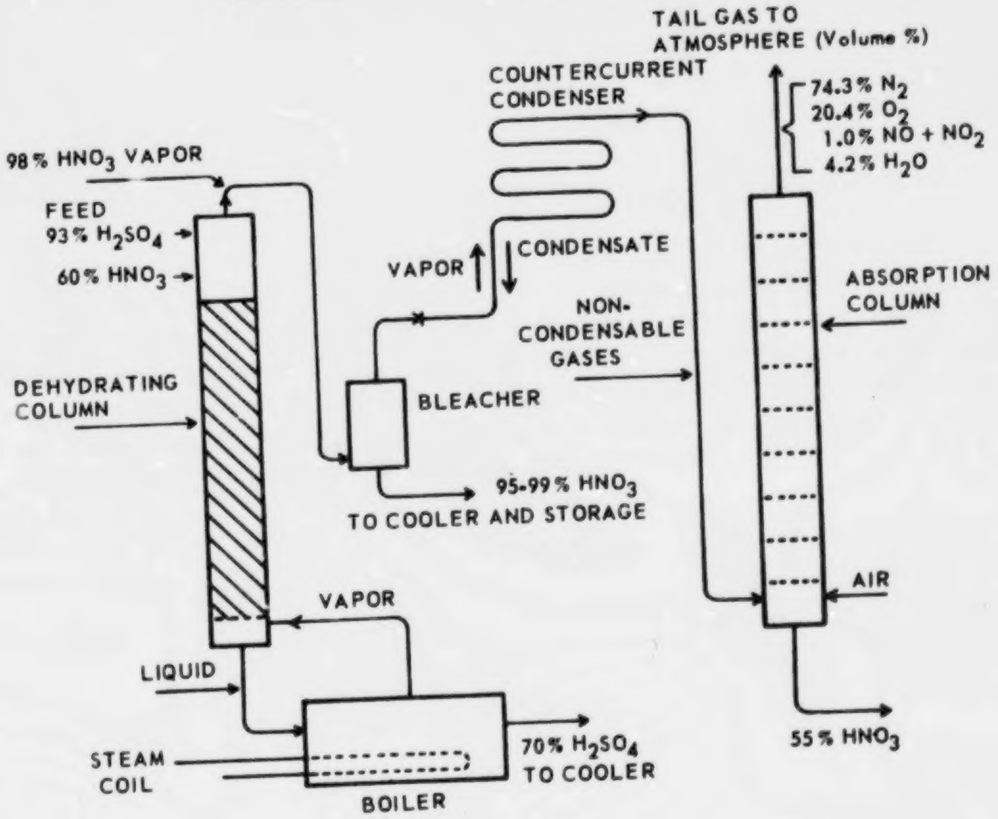

MAIN INLET GAS STREAM
TAIL GAS STREAM
EFFLUENT
⑪
STACK
AMMONIA VAPOR
①
MIXER
AIR
③
AMMONIA OXIDIZER
CATALYST
④
NATURAL GAS
REHEATER
AIR HEATER
CATALYTIC REDUCTION UNIT (for nitrogen oxides abatement)
STEAM
WASTE HEAT BOILER
AIR
②
MOTOR
COMPRESSOR — EXPANDER
STEAM
WASTE HEAT BOILER
PLATINUM FILTER
WATER
COOLER COND.
LIQUID SEPARATOR
⑤
⑥
⑦
⑩
ENTRAINMENT SEPARATOR
WATER
⑨
ABSORPTION TOWER
PRODUCT 55-65% HNO₃
⑧

FIGURE 3-8

NITRIC ACID CONCENTRATING UNIT


TAIL GAS TO ATMOSPHERE (Volume %)
74.3% N₂
20.4% O₂
1.0% NO + NO₂
4.2% H₂O
COUNTERCURRENT CONDENSER
98% HNO₃ VAPOR
FEED
93% H₂SO₄
60% HNO₃
VAPOR
CONDENSATE
NON-CONDENSABLE GASES
ABSORPTION COLUMN
DEHYDRATING COLUMN
BLEACHER
95-99% HNO₃ TO COOLER AND STORAGE
VAPOR
AIR
LIQUID
STEAM COIL
BOILER
70% H₂SO₄ TO COOLER
55% HNO₃

The Hoko process (3-71) differs from other nitric acid processes by making concentrated (98-99%) nitric acid directly. It has found so far very limited application in the U.S., where acid concentrations of 55-65% are satisfactory for the ammonium nitrate production which consumes about 75% of all nitric acid produced. In the Hoko process, ammonia combustion using air or oxygen takes place at atmospheric pressure. The combustion gases are cooled to about 30°C, as rapidly as possible, in order to condense and remove water as dilute nitric acid (1-2% HNO_3). The gas is then compressed and NO is oxidized to NO_2, which is absorbed in cold concentrated nitric acid. The absorber liquid, an N_2O_4-HNO_3 solution, is mixed with the required volume of water, and the mixture is admitted to an autoclave and oxidized with pure oxygen to make 98 or 99% nitric acid. The gas from the absorber is scrubbed with weak acid to remove HNO_3. The NO_x in the tail gas is said to be 0.05% by volume (3-71). A problem is the disposal of the weak acid formed by condensing the ammonia oxidation vapors.

About 5 pounds/ton of nitric acid is emitted in the absorber gas from nitric acid concentration units. Typical NO_x concentration is about 1% (3-69), reflecting operation at essentially atmoepheric pressure. While figures are not available on the volumes of concentrated nitric acid produced (see Section 3.1.4.2) rough estimates of concentrated HNO_3 requirements and resulting NO_x emissions for the U.S. in 1967 are as follows:

TABLE 3-13

Estimates of Strong Acid Requirements and NO_x Emissions from Concentration Operations

Use	Nitric Acid Requirements Total HNO_3 Tons	% Strong Acid	Strong Acid Ton/Yr	NO_x Tons/Yr
Nitrobenzene	90,000	72	65,000	162
Toluene Diisocyanate	75,000	51	38,000	95
Commercial Explosives	38,000	100	38,000	95
Total	203,000		141,000	352

Not included in the numbers above are acid requirements and NO_x emissions from nitric acid concentration operations for producing military explosives.

3.1.4.2. Nitric Acid Uses

Important uses of nitric acid and the estimated quantities consumed in each use are listed in Table 3-14. The bases for these estimates is given in the following discussion.

Table 3-14

Estimated Nitric Acid Consumption in the U.S., 1967

Use	Tons
Ammonium Nitrate	4,540,000
Organic Oxidations	
Adipic Acid	560,000
Terephthalic Acid	100,000
Organic Nitrations	
Nitrobenzene	90,000
Toluene Diisocyanate	75,000
Commercial Explosives (ex NH_4NO_3)	38,000
Fertilizers (ex NH_4NO_3)	150,000
Other Uses	569,000
Total	6,122,000 (3-70)

Approximately 3/4 of U.S. nitric acid production is consumed in making ammonium nitrate, while adipic acid manufacture consumes about 9%. No other single outlet consumes more than about 4%. The "other uses" category includes such outlets as metal pickling and etching, nitrations and oxidations of organic compounds, production metallic nitrates, and many others.

Ammonium Nitrate Manufacture

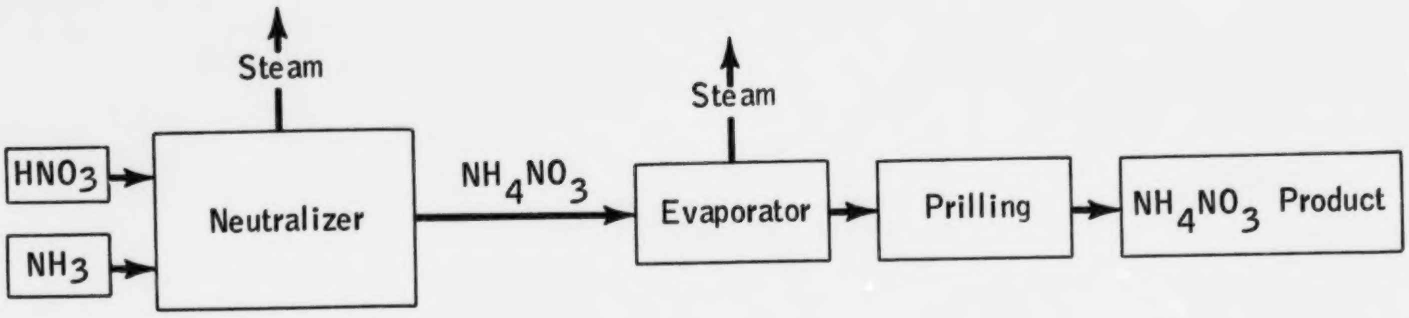
Ammonium nitrate is produced by the direct neutralization of nitric acid with ammonia.

$$NH_3 + HNO_3 \longrightarrow NH_4NO_3 \qquad (3\text{-}4)$$

Figure 3-9 shows a simplified flow plan for making ammonium nitrate prills.

Figure 3-9

BLOCK DIAGRAM FOR MANUFACTURE OF AMMONIUM NITRATE PRILLS



About 0.81 tons of nitric acid (100% equivalent) and 0.210-0.225 tons of anhydrous ammonia are required to make one ton of ammonium nitrate. 100% nitric acid is not used in actual practice, and typical feed acid contains 55-60% HNO_3. The product is an aqueous solution of ammonium nitrate which may be used as liquid fertilizer, or be converted into a solid product. The strength of the solution varies. The heat of reaction is usually employed to evaporate part of the water, giving typically a solution of 83-86% ammonium nitrate.

Further evaporation to a solid may be accomplished in a falling film evaporator(3-72), a disk-spraying plant(3-73), or by evaporation to dryness in a raked shallow open pan (graining)(3-73). The latter method was used through World War II in making explosives.

Much of the solid ammonium nitrate produced in the U.S. is formed by prilling, a process in which molten ammonium nitrate flows in droplets from the top of a tower countercurrent to a rising stream of air. This cools and solidifies the melt, producing pellets or prills(3-72).

In 1967, 5.606 x 10^6 tons of ammonium nitrate were produced(3-70) which, at a nitric acid consumption rate of 0.81 tons/ton of ammonium nitrate, required about 4.54 x 10^6 tons of nitric acid. About 0.7-0.8 x 10^6 tons(3-74) were used in explosives, and most of the remainder in direct application or mixed fertilizers.

No significant amount of NO_x is produced in this process; the most likely source of nitric acid emissions would be the neutralizer, but the vapor pressure of ammonia is much higher than the vapor pressure of nitric acid, and the release of nitric acid fumes or NO_x are believed to be negligible(3-75), especially since a slight excess of NH_3 is used to reduce product decomposition.

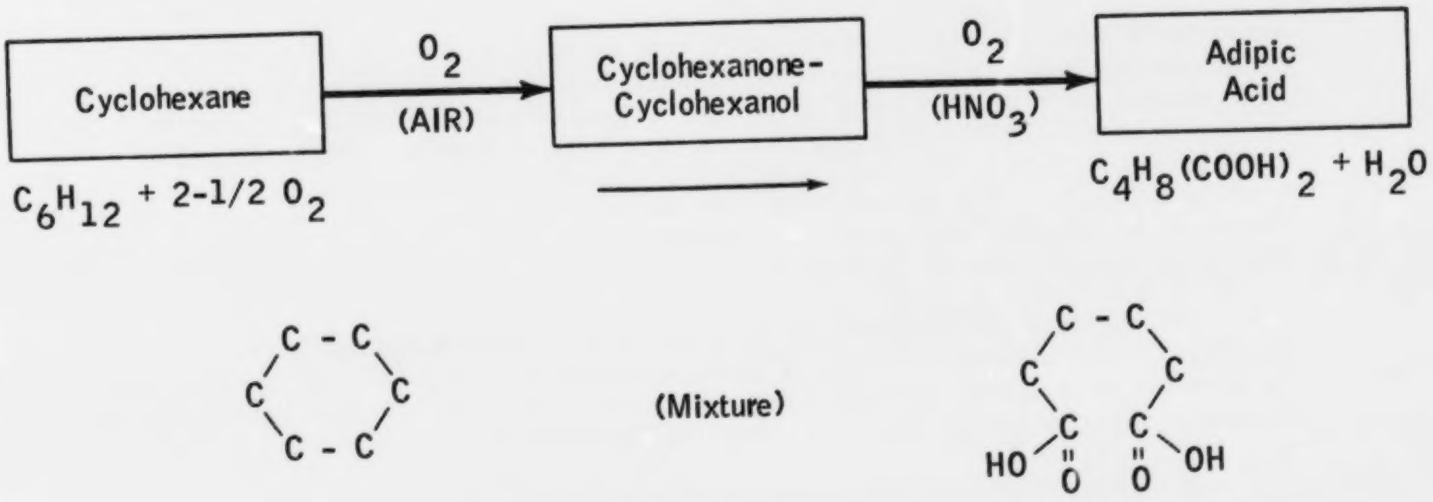
Organic Oxidations

Nitric acid is used as an oxidation agent in the commercial preparation of adipic acid, terephthalic acid, and other organic compounds containing oxygen. The effective reagent is probably NO_2, which has very strong oxidizing power.

Adipic acid, $COOH\cdot(CH_2)_4\cdot COOH$, is a dibasic acid used in the manufacture of nylon. In the U.S., adipic is made in a two-step operation as shown in the diagram below.

Figure 3-10

ADIPIC ACID SYNTHESIS



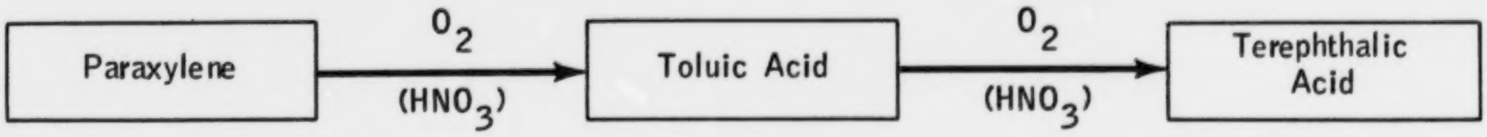
The first step is the catalytic oxidation of cyclohexane by air to cyclohexanol and cyclohexanone. In the second step, adipic acid is made by the catalytic oxidation of the cyclohexanol/cyclohexanone mixture using 45/55% nitric acid. The product is purified by crystallization(3-76). The whole operation is continuous.

In oxidizing cyclohexanol/cyclohexanone nitric acid is reduced to unrecoverable N_2O and potentially recoverable NO and NO_2. According to Lindsay(3-77) the nitric acid requirement is 1.46 pounds/pound of chemically formed adipic acid, 0.43 pounds of which is potentially recoverable NO_x and 1.03 pounds of which is non-recoverable N_2O.

Terephthalic acid is an intermediate in the production of polyethylene terephthalate for use in polyester and films and other miscellaneous products. Some terephthalic acid can be produced in various ways, one of which is by the oxidation of paraxylene using nitric acid. The nitric acid oxidation proceeds in two steps as shown in the Figure 3-11.

Figure 3-11

TEREPHTHALIC ACID SYNTHESIS



$$C_6H_4(CH_3)_2 + 1\text{-}1/2\ O_2 \longrightarrow CH_3C_6H_4\ COOH + H_2O$$

$$CH_3C_6H_4\ COOH + 1\text{-}1/2\ O_2 \longrightarrow C_6H_4(COOH)_2 + H_2O$$

Both steps take place in a single reactor. The first step yields primarily N_2O, while the second step yields mostly NO in the offgas(3-78). Based on the information in reference (3-78), the nitric acid requirement for terephthalic acid is estimated to be 1.33 pounds/pound of terephthalic acid, 0.76 pounds of which is potentially recoverable (NO) and 0.57 pounds is non-recoverable (N_2O).

In 1967, total estimated terephthalic acid production was about 395 thousand tons, an estimated 150 thousand tons of which was made via nitric acid oxidation. Estimated adipic acid production was about 540 thousand tons(3-79) all of which is believed to be made from nitric acid oxidation of cyclohexanol/cyclohexanone. Nitric acid is used for oxidation of other organic compounds in addition to terephthalic acid and adipic acid, but none is believed to approach these two in product volume.

No data are available on NO_x emissions in streams released to the atmosphere from manufacturing operations employing nitric acid as an agent for oxidizing organic compounds. The off gases leaving the reactor after nitric acid oxidation of organic materials may contain as much as 50% NO_x before processing for acid recovery,(3-77, 3-78) N_2O, one of the principal compounds of the off gas, is not counted as NO_x, since it is considered harmless, and is not oxidized to NO_x in the atmosphere.

NO_x emissions and nitric acid requirements were roughly estimated, based on references (3-77, 3-78) and assuming that NO_x in absorber off gas would be reduced to 0.3%, a level typical of nitric acid plants. The absorption system recovers an estimated 98/99% of the NO_x as nitric acid and recycle it back to the unit. The rough estimates are shown in Table 3-15.

Table 3-15

Estimated Acid Requirements and NO_x Emissions From Nitric Acid Oxidation of Organic Compounds, 1967

	Adipic Acid	Terephthalic Acid
Production Rate, Million lb/Yr. (3-79)	1080	300*
Net HNO_3 Consumption Lb./Lb. Product**	1.04	0.68
Net HNO_3 Consumption, Tons/Yr.**	560,000	100,000
NO_x Emissions Lb./Ton Product	11.6	13.0
NO_x Emissions, Tons/Yr.	3000	1000

---

* Terephthalic acid produced by nitric acid oxidation only.

** After crediting for HNO_3 recovered from off gases.

The estimated NO_x emissions from these two sources amount to 0.05% of total NO_x emissions from all stationary sources, or 0.03% of total NO_x emissions from all sources in the U.S.

Organic Nitrations

Nitration is treating organic compounds with nitric acid (or sometimes NO_2) to produce nitro compounds or nitrates. The following equations illustrate the two most common types of reaction:

$$RH + HONO_2 \longrightarrow RNO_2 + H_2O \qquad (3\text{-}5)$$

$$ROH + HONO_2 \longrightarrow RONO_2 + H_2O \qquad (3\text{-}6)$$

Examples of the first reaction are the manufacture of nitrobenzene, nitrotoluenes, and nitromethane. Nitroglycerin (or glyceryl trinitrate) and nitrocellulose are examples of the second reaction.

Nitrating agents used commercially include nitric acid, mixed nitric and sulfuric acids (mixed acids), and NO_2. Mixed nitric and sulfuric acid is most frequently used. The function of the sulfuric acid is to promote formation of NO_2^+ ions, as well as to absorb the water produced in the reaction.

Nitrations are carried out in either batch or continuous processes. The trend is toward continuous, since control is more easily maintained, equipment is smaller, system holdup is smaller, and hazards are reduced. However, there is a multitude of specialty products such as dyes and drugs, produced in small volumes, which will continue to be manufacturered by small batch nitrations.

Batch nitration reactors are usually covered vessels provided with stirring facilities and cooling coils or jackets. The reactor bottom is sloped and product is withdrawn from the lowest point. When products are potentially explosive, a large tank containing water (drowning tank) is provided so that the reactor contents can be discharged promptly and "drowned" in case of abnormal conditions.

Upon completion of the reaction, the reactor contents are transferred to a separator where the product is separated from the spent acid. The product is washed, neutralized, and purified, while spent acids are processed for recovery.

Continuous nitration for nitroglycerin is carried out in many types of equipment. Two processes which are widely employed are the Schmid-Meissner process and the Biazzi process. Both processes provide for continuous reaction, separation, water washing, neutralization, and purification. The Biazzi process makes greater use of impellers for contacting than the Schmid-Meissner, which uses compressed air in washing and neutralizing to provide agitation. Both types of equipment can be used for nitrating in general.

When mixed acid is employed, the spent acid is recovered in the following manner: The mixed acid enters the top of the denitrating tower. Superheated steam is admitted at the bottom to drive off the spent nitric acid and NO_x overhead. The gases pass through a condenser to liquify nitric acid, which is withdrawn to storage, and the uncondensed gases pass to an absorption tower. Weak sulfuric acid is withdrawn from the bottom of the denitrator tower and then concentrated or otherwise disposed of.

When nitric acid alone is used for nitration, the weak spent acid is normally recovered by sending it to an absorption tower, replacing some of the water normally fed as absorbent.

Nitrobenzene and dinitrotoluenes are produced in large volumes as chemical intermediates. Explosives such as TNT, nitroglycerine, and nitrocellulose are produced in significant but lesser volumes. These materials are discussed below.

Nitrobenzene is manufactured in both continuous and batch nitration plants. Mixed acids containing 53-60% H_2SO_4, 32-39% HNO_3, and 8% water are employed in batch operations, which may process 1000-1500 gallons of benzene in 2-4 hours. Continuous plants, as typified by the Biazzi units, also use mixed acids. A 30 gallon continuous nitrator has the capacity of a 1500 gallon batch nitrator. Yields are 95-99% of theoretical (3-81).

The major use of nitrobenzene is in the manufacture of aniline. It is also used as a solvent. Nitrobenzene production in 1967 was an estimated 170,000 tons. Nitric acid requirements are approximately 0.53 pounds per pound of nitrobenzene(3-81). On this basis, estimated nitric acid consumption in making nitrobenzene was 70 thousand tons in 1967.

Dinitrotoluene is manufactured in two stages in both continuous and batch units. The first stage is nitration of toluene to mononitrotoluene, and the mononitrotoluene is nitrated to dinitrotoluene in the second stage (3-82).

Dinitrotoluene's principal use is as an intermediate in making toluene diisocyanate (TDI) for use in polyurethane plastics. It is usually supplied as mixtures of the 2,4 and 2,6 isomers. In 1967, about 200 million pounds of toluene diisocyanate was produced, which required an estimated 75 thousand tons of nitric acid based on 0.74 pounds of nitric acid per pound of TDI.

Relatively large NO_x emissions may originate in the nitration reactor and in the denitration of the spent acid. NO_x is also released in auxiliary equipment such as nitric acid concentrators, nitric acid plants, and nitric acid storage tanks.

Nitration reactions per se do not generate NO_x emissions. NO_x is formed in side reactions involving the oxidation of organic materials. Relatively little oxidation and NO_x formation occurs when easily nitratable compounds are processed, such as toluene. Much more severe conditions are required and more oxidation takes place in processing compounds such as dinitrotoluene which are difficult to nitrate, and more NO_x is formed.

Very few data are reported in the literature on NO_x emissions from nitrations. For continuous nitrations, one company has reported emissions of 0.12-0.24 lb NO_x/ton of nitric acid, with a mean of 0.18 at a single location(3-83). At the same location emissions averaging 14 pounds per ton of acid were reported in manufacturing specialty products in small batch-type operations. Further discussion of these small batch nitrations appears in the emission controls section.

Using the factors 0.14 and 14 lb NO_x/ton HNO_3 as lower and upper limits for nitrations the NO_x emissions would have the following range in 1967.

Table 3-16

Estimated NO_x Emissions From Organic Nitrations in 1967

	Est. Acid Consumption Tons/Year	NOx, Tons/Year Lower Limit	NOx, Tons/Year Upper Limit
Nitrobenzene	90,000	8	630
Dinitrotoluene	75,000	7	530

Even using the upper limit, NO_x emissions from making nitrobenzene and dinitrotoluene are relatively small but may present local nuisance problems. Since the upper limit represents specialty batch operations on a small scale, the emissions are probably much higher than would be encountered in large volume production of these products in either batch or continuous equipment.

Explosives, Manufacture and Use

Industrial explosives in the United States consist of over 80% by weight of ammonium nitrate and some 10% of nitro organic compounds The following estimates of ingredients used in commercial explosives were derived from statistics of the U.S. Bureau of Mines(3-84).

Table 3-17

Ingredients in U.S. Industrial Explosives, 1967

	Tons
Ammonium Nitrate	
Processed & Unprocessed	643,000
In Permissibles*	23,000
In other High-Explosives*	53,000
In other Blasting Agents*	76,000
Total Ammonium Nitrate	795,000
Fuel Oil, Carbonaceous Material & Other Non-explosive Ingredients	120,000(a)
Nitroglycerin	28,000(a)
TNT	10,000(a)
TOTAL	953,000

---

* Ammonium nitrate estimated at 65% of permissible, 35% of other high explosives and 60% of water gels and slurries and rigidly cartridged blasting agents (3-85, 3-86).

(a) Estimates provided by DuPont (3-92).

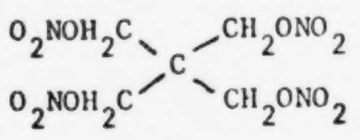
Ammonium nitrate (AN) is widely used because it is the least costly of all explosives, it is very powerful, and it is low in relative hazard. Smaller amounts of other explosives such as nitroglycerin (NG) and trinitrotoluene (TNT) were consumed in commercial explosives in 1967. The manufacture of ammonium nitrate has been discussed above. The manufacture of TNT is included below under military explosives.

Nitroglycerin is manufactured in one stage in both batch and continuous units using mixed acids. Description of specific batch and continuous units are included in the general description of nitration above. Anhydrous mixed acid containing 45-50% HNO_3 and 50/55% H_2SO_4 is the most common nitrating agent. Nitric acid consumption is about 1 pound per pound of nitroglycerin(3-87). TNT also requires about 1 pound of nitric acid per pound of product(3-82). The estimated consumption of nitric acid in 1967 in commercial explosives other than ammonium nitrate, was 38,000 tons based on the 38,000 tons of TNT plus nitroglycerin as derived above.

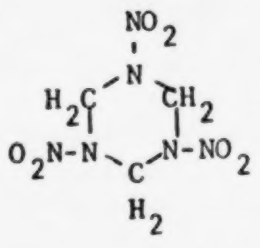
Military explosives production and consumption data are classified. Some of the more important ingredients in military explosives are TNT, penterythritol tetranitrate (PETN) cyclotrimethylenetrinitramine (RDX) and trinitrophenylmethylnitramine (tetryl). Nitration is an essential step in the manufacture of each of these.

The formulas for PETN, RDX and Tetryl are shown below:

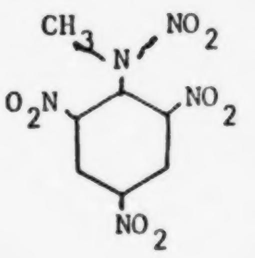
PETN



RDX



Tetryl

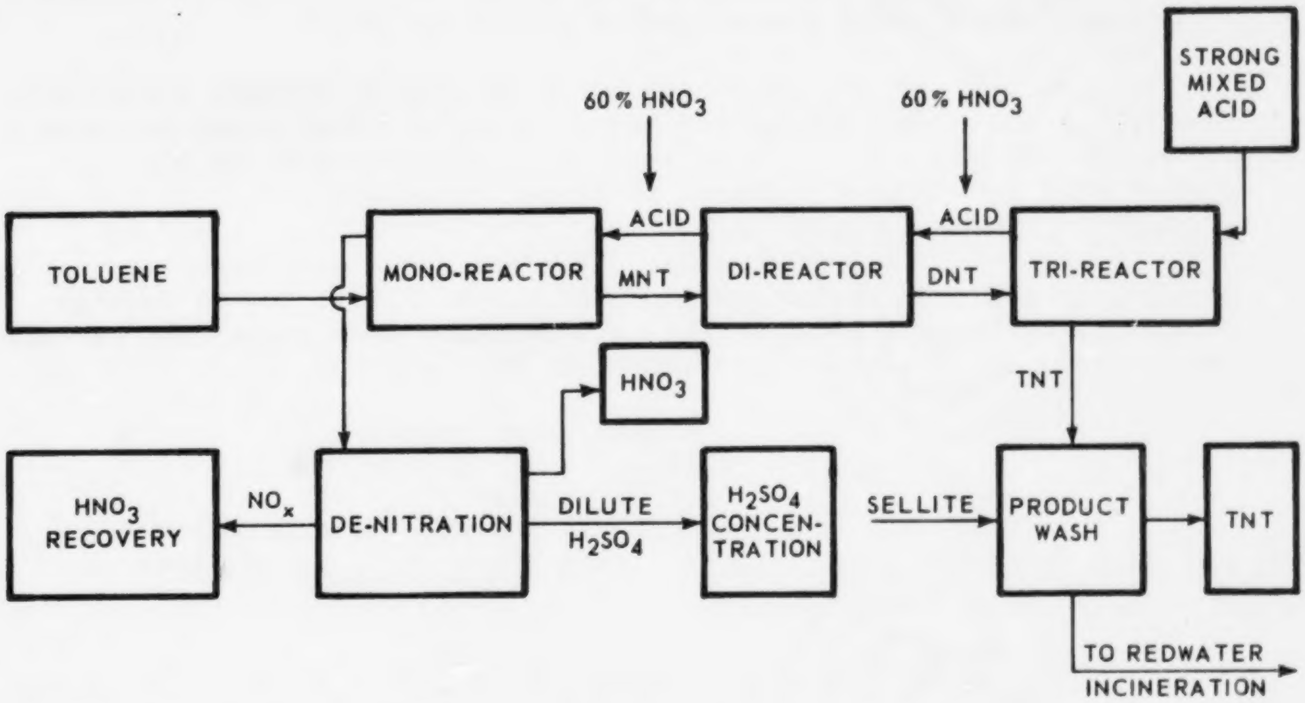


PETN is most commonly used in conjunction with TNT in the form of pentolites, made by incorporating PETN into molten TNT. RDX is used in admixture with TNT, or compounded with mineral jelly to form a useful plastic explosive. Tetryl is most often used as a primer for other less sensitive explosives. Methods of preparation of these explosives are discussed in detail by Urbanski(3-82).

TNT (symmetrical trinitrotoluene) is produced in batch and continuous processes. The addition of each successive nitro group to the toluene molecule becomes more difficult, so that more severe conditions are required. Therefore, it is normal practice to introduce strong mixed acids at one end and toluene at the other in a multistage-operation as illustrated in Figure 3-12.

FIGURE 3-12

TNT MANUFACTURING DIAGRAM


STRONG MIXED ACID
60% HNO_3
60% HNO_3
ACID
ACID
TOLUENE
MONO-REACTOR
MNT
DI-REACTOR
DNT
TRI-REACTOR
HNO_3
TNT
HNO_3 RECOVERY
NO_x
DE-NITRATION
DILUTE H_2SO_4
H_2SO_4 CONCEN-TRATION
SELLITE
PRODUCT WASH
TNT
TO REDWATER INCINERATION

The spent acid leaving one stage is fortified with fresh nitric acid before entering the next stage. The spent acid from the final stage is denitrated. Nitric acid is recovered from the denitrator overhead, for recycling to the process and the uncondensable gas is sent to an absorption tower to recover NO_x as nitric acid.

TNT is purified by washing with sodium sulfite (Sellite). The principal impurities are unsymmetrical trinitrotoluenes, which react rapidly with sodium sulfite to form dinitrotoluene sulfonates, which are soluble in the wash water. The waste wash water is disposed of by evaporation, the residue being incinerated(3-82). The waste water has a deep red color from the nitro compounds and is generally referred to as "redwater".

Operating conditions for nitrating dinitrotoluene to trinitrotoluene are severe--anhydrous mixed acid, and temperatures of 100°C and higher. Yields of 82-90% of theoretical are typical, due to oxidation reactions which generate carbon oxides and NO_x(3-82). Therefore, it is essential to process the reactor fumes as well as denitrator uncondensibles in an absorption tower, to minimize net acid consumption.

For discussion on the various processes used manufacturing TNT, the reader is referred to Urbanski's book(3-82).

NO_x emissions from TNT nitration reactors at the new Ordnance Works at Newport, Indiana, have been estimated at approximately 2.5 pounds per ton of TNT. The NO_x concentration, after dilution with 14 volumes of air prior to release, was estimated at 400 ppm(3-93).

Much higher NO_x emissions were reported at another ammunition plant where the equipment was old and overloaded. This plant has been an intense source of NO_x, generating about 130,000 pounds of NO_x/day (3-88, 3-89). A program is planned to reduce emissions.

Assuming that the average TNT plant would emit twice as much NO_x as the new plant mentioned above, and that no NO_x is emitted in nitroglycerin manufacture(3-92), NO_x emission from commercial explosives (see Table 3-17) are roughly estimated as follows:

Table 3-18

Nitric Acid Requirements and NO_x Emissions From Manufacturing Industrial Explosives, U.S. Total, 1967

	Product Tons	HNO_3 Tons	NO_x Lb/Ton HNO_3	NO_x Tons/Yr.	Ton NO_x/Ton of Product
TNT (industrial use)	10,000	10,000			
Reactor			5.0	25	0.003

Redwater destruction is not employed in manufacturing TNT for commercial use(3-92).

Other sources of NO_x related to explosives manufacturing are denitration of spent mixed acid, nitric acid concentrators, and nitric acid production.

At the Newport plant, emission from denitration and nitric acid concentration were estimated at about 12 pounds per ton of nitric acid after 75% reduction in a fume burner. The NO_x concentration was estimated at 1.7%, probably all NO.

Oxygen balance is the most important factor affecting the NO_x content of the products of explosions. An oxygen balanced explosive contains just enough oxygen to oxidize all the carbon in the explosives to carbon dioxide and all hydrogen to water. A deficiency of oxygen produces toxic carbon monoxide while an excess of oxygen tends to produce NO_x (3-85,3-86). Ammonium nitrate itself contains an excess of one atom of oxygen per molecule. Combustible materials, e.g., 5% fuel oil, are usually added to ammonium nitrate to provide oxygen balance and increase power. Nitroglycerin has a slight oxygen surplus, while TNT is short of oxygen.

Compositions of the products of explosions are difficult to measure. For this reason, most of the information on these products is obtained by detailed computer calculations. The reader is referred to Cook's book for information on methods of calculations(3-85). NO_x is found in explosion products when the explosive contains more oxygen than required for oxygen balance. Calculated NO_x in products from various explosives are listed in Table 3-19.

Table 3-19

NO_x in Products of Explosions

	NO_x	
	%	lbs/Ton Explosives
TNT, 50/50 Amatol, RDX, Tetryl, Straight dynamites, AN-Fuel Oil	0	0
AN/DNT	0	0
PETN	0.3-0.6	10-18
Nitroglycerin	1.5	46
Straight Gelatins, 40%	0.1	3
75%	0.1	3

The volume of NO_x generated in commercial explosions in 1967 was probably less than 100 tons since most of the 28 thousand tons of nitroglycerin was consumed in oxygen-balanced explosives(3-92).

Thus, explosions are a very small source of NO_x emission but could be an intense source in confined spaces underground, and precautions should be taken to avoid exposure in such places.

Other Uses of Nitric Acid

Other uses of nitric acid include acidulation of phosphate rock and limestone for making fertilizer, metals treating, and rocket fuel oxidation.

Fertilizer

In the U.S. sulfuric and phosphoric acids are the principal acids used in acidulating phosphate rock. However, a few manufacturers produce "nitric phosphate" fertilizers by acidulating phosphate rock with nitric acid to form phosphoric acid and calcium nitrate. In subsequent steps, ammonia and either sulfuric or phosphoric acid or carbon dioxide are added, and "nitric phosphates" are formed. Dibasic calcium phosphate and ammonium nitrate are the useful products(3-90).

U.S. Department of Agriculture statistics(3-91) do not segregate fertilizers made for nitric acid acidulation of phosphoric rock, but from private sources, nitric phosphate fertilizer made in this manner was estimated at 500,000 tons in 1967, and nitric acid consumption at 150,000 tons.

NO_x emissions are dependent on the quantity of carbonaceous material in the rock, NO_x is formed as nitric acid oxidizes the carbonaceous matter. The use of calcined rock avoids the production of NO_x.

Metals Pickling

Nitric acid's principal use in metals pickling is in treating stainless steel. Mill scales on stainless steels are hard and difficult to remove. Pickling procedures vary. Sometimes a 10% sulfuric acid bath at 140-160°F followed by a bath at 130-150°F with 10% nitric acid and 4% hydrofluoric acid are used. The first bath loosens the scale and the second removes it. A continuous system for stainless steel strip consists of two tanks containing 15% hydrochloric acid followed by a tank containing 4% hydrofluoric and 10% nitric acid at 150-170°F. An effective method is the use of molten salts consisting of sodium hydroxide to which is added some agent such as sodium hydride. This may be followed by a dilute nitric acid wash(3-54).

Nitric acid is preferred to other acids in treating stainless steel because it does not attack the steel itself. Sulfuric and hydrochloric acid are usually preferred for other metals, because they are less costly.

No measurements were found of emission rates from nitric acid pickling of stainless steel.

Nitric acid is also used in chemical milling of copper or iron from metals which are not chemically attacked by nitric acid and for bright dipping copper. In the latter operation, a cold solution of nitric and sulfuric acid has been customarily used.

A small, but intense, source of NO_x occurs in the manufacture of tungsten filaments for lightbulbs. Tungsten filaments are wound on molybdenum cores, and after heat treating, the cores are dissolved in nitric acid.

3.1.5 Minor Sources

Refractory Fibers

The production of fibers such as mineral and glass wool requires the melting of refractory material (3000°F). The molten material is reduced to a stream of globules by passage through a strong blast of highly superheated steam or air. The flying molten globules develop and trail long fibrous tails.(3-4)Although more details and other processes are involved, this is essentially the means of producing rock wool and similar mineral fibers. When assembled into batts, etc., the material is widely used for insulation purposes. Production of alumina-silica fibers is of the order of 8 to 10 million lbs/year.(3-93)

No specific data are available on NO_x emissions.

Perlite Expanding Furnaces

Perlite is a glassy volcanic rock which occurs as spherical particles. On rapid heating, the water which they contain causes the spherules to puff up or expand, producing a white cellular low density material.(3-4) In 1967 some 357,560 tons were produced(3-4) of which roughly 90% was used as an aggregate in plaster and concrete. Essentially all furnaces are heated with natural gas. The temperature required is in the range of 1450 to 1800°F. A value of 19 ppm of NO_x has been found in the exhaust gases of one furnace, (3-9 equivalent to 0.065 lb. $NO_x/10^6$ Btu. (3-9)

Baking and Drying Ovens

Ovens for baking and drying are used for such diverse operations as bakery ovens, sand core ovens for foundries, paint baking ovens, plastic curing ovens, and rock wool drying ovens.(3-4)These may be direct fired, in which case the combustion products are in contact with the material being heated, or indirect fired in which air is heated and then circulated through the oven.

Ovens of this type vary considerably in size, design and construction. Some are oil fired but gas is usually preferred. Preheat of the combustion air is not required as operating temperatures are usually in the range of 180-650°F. Combustion gases are discharged directly to the atmosphere unless they contain fumes that require use of an afterburner. Although there may be a relatively large number of such ovens in use, their average hourly heat requirement is low, being possibly of the order of 1.2 million Btu. Available NO_x stack emission has been reported as in the range of 10 to 40 ppm, equivalent to a range of about 0.03 to 0.11 lb. $NO_x/10^6$ Btu gross heating value. (3-9)

Spray Dryers

In spray drying a highly dispersed liquid is contacted with a high temperature gas. The hot gases are usually obtained from a direct fired gas or oil heater. If a controlled atmosphere is necessary, indirect heating is required. A cyclone separator is frequently used to separate the dried produ from the hot gases.(3-4)

The detergent industry is a large user of spray dryers. The heat requirement of such dryers is of the order of 15 million Btu/hour and the NO_x content of the stack gas has been reported at about 7 ppm equivalent to 0.085 lb. $NO_x/10^6$ Btu. (3-9)

Welding

The high temperatures involved in electric arc and oxyacetylene welding (3500°F) are expected to favor NO_x production. Measurements made under conditions of restricted ventilation have shown amounts of NO_x varying from a trace to nearly 35 ppm depending on the particular operation and the conditions involved. These samples were taken at a distance of 6" from the arc and were in the visible fume stream.(3-94) It is estimated that welding operations, in the U.S. overall, contribute roughly 70 tons of NO_x/year to the atmospheric burden. This assumes 10 CF/min of gas, 10 ppm of NO_x, and L.A. data as typical for U.S.

High temperature flames of small size are expected to be similar in NO_x production and usually involve oxygen fortification. Bench type glass blowing and quartz working as well as the recent popular use of flame photometry as an analytical tool are examples.

Electrostatic Precipitators

Extensive use is made of electrostatic precipitators for removal of very small particulate material from gases. The equipment essentially consists of a series of electrodes which, because of their high voltage (20,000 to 100,000 volts in single-stage units) create a corona discharge that ionizes gas molecules and electrically charges the particles passing through the field. The charged particles then tend to migrate toward oppositely-charged surfaces and are removed from the gas stream. It is suggested that the corona discharge forms ozone and atomic oxygen, which can react with nitrogen to form nitrogen oxides.

Certain data from precipitators tied to coal fired steam boilers indicate that such formation of NO_x does occur and other equally acceptable data can be selected to show a decrease in NO_x on passage through an electrostatic precipitator. This marked disagreement in results (which may be related to the operating mode of the precipitator, e.g., arcing instead of corona discharge) has not been explained, and additional information of interest may be developed by further research. Until more reliable information is available, one cannot consider electrostatic precipitation as a contributor of NO_x emissions.

High-Level Exposure in Agriculture

A non-combustion source of nitrogen dioxide that has caused at least several deaths and varying degrees of permanent injury is the gas formed in silos in the first few days after filling.(3-95) Anaerobic bacterial action occurring in the green fodder produces nitrogen dioxide in sufficient quantities to impart a readily visible color. Such a concentration is expected to considerably exceed 40 ppm based on the formula for minimum visibility - 2400/path length in inches = ppm NO_2(3-96)-in which a 5 foot path is assumed. A one-minute exposure to 50 ppm of NO_2 was found to cause chest pains in 30% of human subjects tested.(3-97)

3.2. EMISSION FACTORS, THEIR ACCURACY AND USE

The accuracy of emission estimates calculated from fuel combustion data will depend upon the accuracy of the fuel quantity figure as well as upon the accuracy of the emission factor used in the calculation. It is important to recognize that the development of accurate NO_x emission factors is very difficult due to the complex nature of nitrogen oxide formation from combustion processes.

With NO_x, there is no convenient way of anticipating the approximate amount of pollutant formed from a given amount of fuel, as there is with the oxides of sulfur. The formation of SO_x is directly related to the concentration of sulfur in the fuel. On the other hand, NO_x is formed in substantial concentrations of several hundred ppm or more without chemically bound nitrogen in the fuel, e.g., in natural gas combustion (see Section 4.1.).

The amount of NO_x emitted depends upon a complex set of combustion conditions, equipment design, and operating variables such as installation size, type of burner, cooling surface area, firing rate and air/fuel ratio, as discussed in Section 4. Consequently, the determination of accurate emission factors to represent "average" or "typical" emissions from each class of equipment requires a complicated sampling problem involving selection of representative equipment and testing at representative operating conditions. The quotation below, taken from Report No. 3 of the Joint Los Angeles County report (3-9) concerning NO_x emissions from the single most important emission source, steam power plants, succinctly illustrates these problems.

"In the determination of an NO_x emission factor for power plants, some 130 tests including 554 individual samples were considered. The Department of Water and Power of the City of Los Angeles has been making an extensive study of the effect of operating variables on NO_x emissions. These studies have included a testing program in which two to three tests per week were performed for a period greater than a year."

"The rates of emission of NO_x from units as complex as these, with the possibility of a number of constantly fluctuating operating variables, may be assumed to be constantly fluctuating also. In these circumstances, the rate of emission of NO_x at any given instant in any plant may be different from the rate of emission at the next instant. Experience gained during the carrying out of the project has shown these assumptions to be true. A striking example of this variability is the fact that samples taken as nearly at the same time as possible from two probes in as close proximity to each other as possible show two different values for NO_x concentrations. It was found that actual rates of NO_x emission from sister units may be different for operating conditions which are the same for each unit within the limits of ability to determine. This phenomenon has been verified repeatedly."

"Thus, it may be seen that in the development of an emission factor, calculations must be based on averages of many data taken under many different conditions. As pointed out in the discussion of asphalt paving plants, the use of such a factor to determine the rate of NO_x emission from a single unit at any given time may produce data which are far from reliable for the conditions existing at that time."

"During the carrying out of the test program on power plant boilers, a number of phenomena were brought to light. Instead of clarifying the situation, many of these observations served merely to point up the complexity of the problems. It should be borne in mind that the examples and curves shown are in each case for some particular unit and should not be construed to be correction factors for measured emission rates from any other unit. The degree and direction of the effect of operating variables upon NO_x production must be determined individually for each particular unit to be considered."

In this joint Federal, State, County, and Industry project Mills et al., measured NO_x emissions from a wide variety of gas- and oil-fired combustion equipment, ranging from domestic heaters to large steam boilers, and were able to establish the general relationship between gross heat input and NO_x reproduced in Figure 3-13(3-9). The experimental data they obtained are in many cases the best, or the only actual measurements reported in the literature.

Wide variations from these curves are to be expected for individual units, depending upon specific fuels, operating conditions and equipment design. The top end of the curves is not valid for some measured cases (above 2×10^9 BTU/hr). However, rough estimates of NO_x emissions from a variety of combustion equipment can be made from these curves, if the fuel combustion rate is known. NO_x emission factors from these and other sources have been compiled by Duprey (3-10).

Emission factors for the most part, have been used to represent average emission rates for a particular type of fuel for a particular consumption factor. If no adjustments are made in these factors for specific changes in type and size of equipment, operating rates, and control equipment over a period, they may well misrepresent current emissions.

In some instances, emission factors used in this document do not agree with those published by Duprey (3-10). Such differences have been noted and explained in the description of emission factors for catalytic cracking regenerators and CO boilers, in Section 3.1.2.; the emission factors for open burning appear unreasonable, as discussed in Section 3.1.3.3. In other instances, emission factors were derived from published or unpublished data for use where no published emission factors were to be found: examples are emission factors for cement kilns and lime kilns, and iron ore sintering, coke ovens, and steam coke ovens, and steel soaking pits.

Figure 3-13

ESTIMATED AVERAGE NO_x EMISSIONS FROM SIMILAR PIECES OF COMBUSTION EQUIPMENT (3-9)

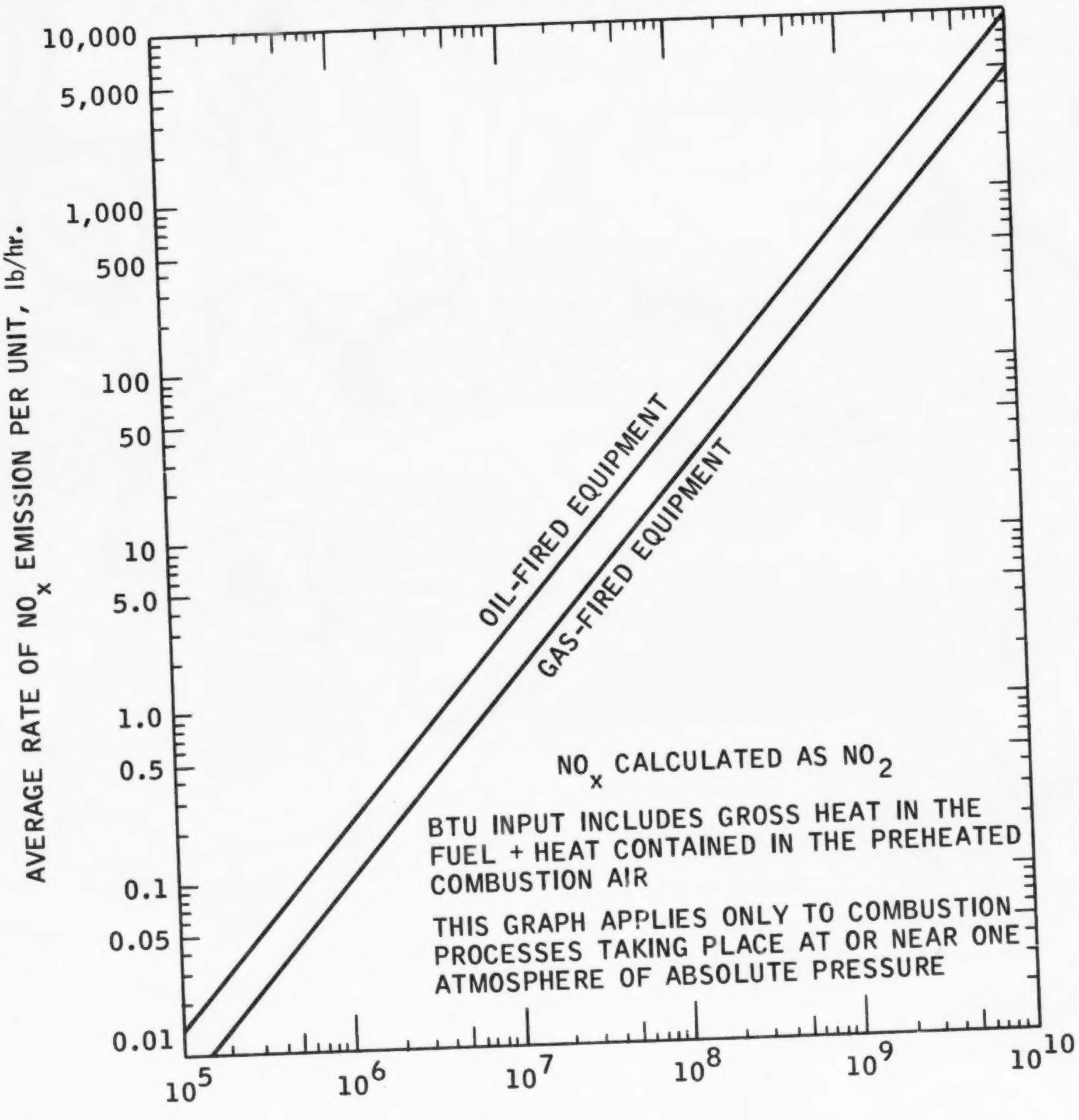


Table 3-20 is a compilation of average NO_x emission factors as used in this study. These factors are based primarily on Duprey's Compilation (3-10) and on values derived in this study. Examples of how these factors may be used are given in Table 3-21. These emission rates represent uncontrolled sources unless otherwise noted. For an operation where control equipment is utilized, the emission rate given for an uncontrolled source must be adjusted for control efficiency.

Table 3-20

Emission Factors for Nitrogen Oxides(1)

Source	Average Emission Factor
Coal	
Household and Commercial	8 lb/ton of coal burned
Industry	20 lb/ton of coal burned
Utility	20 lb/ton of coal burned
Fuel Oil	
Household and Commercial	12-72 lb/1000 gal of oil burned
Industry	72 lb/1000 gal of oil burned
Utility	104 lb/1000 gal of oil burned
Natural Gas	
Household and Commercial	116 lb/million c.f. of gas burned
Industry	214 lb/million c.f. of gas burned
Utility	390 lb/million c.f. of gas burned
Gas Engines	
Oil and Gas Production	770 lb/million c.f. gas burned
Gas Plant	4300 lb/million c.f. gas burned
Pipeline	7300 lb/million c.f. gas burned
Refinery	4400 lb/million c.f. gas burned
Gas Turbines	
Gas Plant	200 lb/million c.f. gas burned
Pipeline	200 lb/million c.f. gas burned
Refinery	200 lb/million c.f. gas burned
Waste Disposal	
Open Burning	11 lb/ton of waste burned
Conical Incinerator	0.65 lb/ton of waste burned
Municiple Incinerator	2 lb/ton of waste burned
On Site Incinerator	2.5 lb/ton of waste burned
Fuel Combustion (Mobile Sources)	
Gasoline-Power Motor Vehicle	113 lb/1000 gal gasoline burned
Diesel-Powered Vehicle	222 lb/1000 gal oil burned
Aircraft: Conventional Jet	23 lb/flight/per engine
Fan-Type Engine	9.2 lb/flight/per engine
Chemical Industries	
Nitric Acid Manufacture	57 lb/ton HHO_3 product
Adipic Acid	12 lb/ton product
Terephthalic Acid	13 lb/ton product
Nitrations	
Large Operations	0.2-14 lb/ton HNO_3 Used
Small Batches	2-260 lb/ton HNO_3 Used

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(1) For NO_x emissions from catalytic cracking regenerations, and CO boilers, see Table 3-6, and the discussion in Section 3.1.2.

Table 3-21

Examples of How to Use The Emission Factors

1. Fuel oil combustion.

   Given: Power plant burns 50,000,000 gals. of fuel oil per year.

   $$50{,}000{,}000 \times \frac{104}{1000} = 5{,}200{,}000 \ \frac{\text{lbs. } NO_x}{\text{yr}}$$

2. Solid waste disposal.

   Given: Conical incinerator burns 7,000 tons of waste per year.

   $$7{,}000 \times 0.65 = 4{,}550 \ \frac{\text{lbs } NO_x}{\text{yr}}$$

3. Process industries

   Given: A certain large continuous nitration employs 40 tons per day of strong HNO_3. If the control device is 90% efficient, what is the daily evolution of NO_x?

   say emission factor = 12 lb/ton HNO_3 used

   $$40 \times 12\ (1.0-0.9) = 48 \ \frac{\text{lbs. } NO_x}{\text{day}}$$

3.3 ESTIMATES AND FORECASTS OF NO_x EMISSIONS

Estimates of the magnitude and character of the NO_x control problem from emission sources have been determined for the years 1950, 1955, 1960, 1965, 1970, 1975, 1980 and 2000. Tables 3-22 through 3-29 provide these data on total United States NO_x emissions by major sectors (household and commercial, industry ex pipeline and gas plant , pipeline and gas plant, electric generation and transportation), by fuel source (natural gas; liquefied gases; kerosene, distillate and residual fuel oils; coal and tar liquids; refuse burning; gasoline; jet fuel; by-product fuels in steel industry) and non-combustion sources.

The tables for past years, 1950-1965, have been calculated largely from published data on fuel consumption and published emission factors, with our own estimates added where necessary, as shown by the footnotes in each table. The fuel quantities are taken largely from Morrison and Readling's Bureau of Mines Information Circular 8384, "An Energy Model for the United States, Featuring Energy Balances for the Years 1947 to 1965 and Projection and Forecasts to the Years 1980 and 2000."(3-12)

The basic energy model developed in Information Circular 8384 is based on data published in the Annual Issues of the U.S. Department of the Interior Minerals Yearbook, Vol. II Fuels, covering the period 1947 to 1965. These data are supplemented by data for the electric utility sector from the United States Federal Power Commission; for the nuclear power industry from the U.S. Atomic Energy Commission and for electricity sales and distribution from the annual issues of the Edison Electric Institute Statistical Yearbook. Historical data on energy demand by major industry groups were obtained from the U.S. Department of Commerce Census of the Mineral Industries and the Census of Manufacturers for the Census Years 1947, 1954, 1958 and 1962.

The forecasts in Information Circular 8384 include integrated energy balances for the years 1980 and 2000 giving the type, source and amount of energy used by each major consuming sector. This presented a useful starting point for developing our NO_x forecasts. Base cases representing a median-range level of demand for total energy the years 1980 and 2000 were calculated by relating the components of total demand to projected trends, for a number of relevant determining variables. For example, the total energy demand is related to Gross National Product (GNP), the household and commercial sector is projected with population growth, and the industrial sector with a composite variable representing industrial production. The 1964 Federal Power Commission National Power Survey data were used for making Electric Utility projections. Trends in efficiency have been taken into account, and continuation of current trends in interfuel competition and substitution within energy markets have been assumed.

TABLE 3-22

ESTIMATED NO_x EMISSIONS FOR YEAR 1950

United States

Fuel Source	Household and Commercial	Industry Ex Pipeline and Gas Plant	Pipeline and Gas Plant(8)	Electric Generation	Total Stationary	Transportation	Grand Total
Natural Gas(1)-10^9 Ft^3 (10^{12} BTU)	1,568 (1,642)	2,937 (3,040)	380 (394)	629 (651)			
Tons $NO_x/10^9$ Ft^3	58(2)	165(7)	1,729(7)	195(2)			
Tons NO_x	91,000	402,000	657,000	123,000	1,273,000	--	1,273,000
Liquefied Gases(1)-10^6 BBl (10^{12} BTU)	54.4 (218)	89 (522)					
Tons $NO_x/10^6$ BBl							
Tons NO_x	12,000(3)	69,000(3)			81,000		81,000
Fuel Oil; Kerosene Distillate & Residual(1) 10^6 BBl (10^{12} BTU)	406.2 (2,385)	301		106.3 (662.2)		261 (1,607)	
Tons $NO_x/10^6$ BBl	617(6)	1,664(7)		2,184(2)		4,660(2)	
Tons NO_x	251,000	501,000		232,000	984,000	1,216,000	2,200,000
Coal + Lignite(1)-10^6 Tons (10^{12} BTU)	115 (3,028)	115 (3,008)		92		64 (1,700)	
Tons $NO_x/10^6$ Tons	4,000(2)	10,000(2)		10,000(2)		10,000(2)	
Tons NO_x	460,000	1,150,000		920,000	2,530,000	640,000	3,170,000
Refuse Burning(4)-10^6 Tons	66	28					
Tons $NO_x/10^6$ Tons	738(2)	738(2)					
Tons NO_x	49,000	21,000			70,000		70,000
Gasoline(1)-10^6 BBl (10^{12} BTU)						1,007 (5,256)	
Tons $NO_x/10^6$ BBl						2,373(2)	
Tons NO_x						2,389,000	2,389,000
Jet Fuel(1)-10^6 BBl (10^{12} BTU)							
Tons $NO_x/10^6$ BBl							
Tons NO_x						6,000(5)	6,000
By-Product Fuels in Steel Industry		188,000			188,000		188,000
Total from Combustion - Tons NO_x	863,000	2,331,000	657,000	1,275,000	5,126,000	4,251,000	9,377,000
Non-Combustion Sources		50,000			50,000		50,000
				GRAND TOTALS	5,176,000	4,251,000	9,427,000

(1) W. E. Morreson and C. L. Reading, "An Energy Model for the United States, Featuring Energy Balances for the Years 1947 to 1965 and Projections and Forecasts to the Year 1980 and 2000." IC 8384 - 1968. U.S. Dept. of Int. Bu. of Mines.

(2) R. L. Duprey, "Compilation of Air Pollutant Emission Factors," U.S. Dept. of H.E.W. P.H.S. Publ. No. 999-AP-42, 1968.

(3) Calculated on a BTU basis using natural gas emission factor - i.e. (218/1642) x 91,000 = 12,000 Tons NO_x.

(4) Calculated as 3.4 lb. refuse per capita day (70% household and commercial -30% industrial).

(5) Assumed 20 lb. NO_x per Flight. Based on Estimated Passenger-Miles. (Resources in America's Future Inc.)

(6) Weighted emission factor based on 71% Household fuel and 29% Commercial fuel used in 19 APC areas with 50,000,000 population.

(7) Composite Emission Factor calculated from Table 3-30.

(8) Pipeline = 475,000 Tons NO_x; Gas Plant = 183,000 Tons NO_x.

TABLE 3-23

ESTIMATED NO_x EMISSIONS FOR YEAR 1955

United States

Fuel Source	Household and Commercial	Industry Ex Pipeline and Gas Plant	Pipeline and Gas Plant(8)	Electric Generation	Total Stationary	Transportation	Grand Total
Natural Gas(1)-10^9 Ft^3 (10^{12} BTU)	2,753 (2,850)	4,195 (4,342)	485 (502)	1,153 (1,194)			
Tons $NO_x/10^9$ Ft^3	58(2)	127(7)	1,730(7)	195(2)			
Tons NO_x	160,000	533,000	839,000	225,000	1,757,000		1,757,000
Liquefied Gases(1)-10^6 BBl (10^{12} BTU)	72 (288)	129(9) (749)					
Tons $NO_x/10^6$ BBl							
Tons NO_x	16,000(3)	92,000(3)			108,000		108,000
Fuel Oil:Kerosene Distillate & Residual(1) 10^6 BBl (10^{12} BTU)	527 (3,098)	348		82 (512)		301 (1,824)	
Tons $NO_x/10^6$ BBl	617(6)	1,635(2)		2,184(2)		4,660(2)	
Tons NO_x	325,000	569,000		179,000	1,073,000	1,403,000	2,476,000
Coal + Lignite(1)-10^6 Tons (10^{12} BTU)	71 (1,898)	102 (2,883)		144 (3,484)		18 (474)	
Tons $NO_x/10^6$ Tons	4,000(2)	10,000(2)		10,000(2)		10,000(2)	
Tons NO_x	284,000	1,020,000		1,440,000	2,744,000	180,000	2,924,000
Refuse Burning(4)-10^6 Tons	80	34					
Tons $NO_x/10^6$ Tons	738(2)	738(2)					
Tons NO_x	59,000	25,000			84,000		84,000
Gasoline(1)-10^6 BBl (10^{12} BTU)						1,363 (7,307)	
Tons $NO_x/10^6$ BBl						2,373(2)	
Tons NO_x						3,234,000	3,234,000
Jet Fuel(1)-10^6 BBl (10^{12} BTU)							
Tons $NO_x/10^6$ BBl							
Tons NO_x						10,000(5)	10,000
By-Product Fuels in Steel Industry		210,000			210,000		210,000
Total from Combustion - Tons NO_x	844,000	2,449,000	839,000	1,844,000	5,976,000	4,827,000	10,803,000
Non-Combustion Sources		98,000			98,000		98,000
				GRAND TOTALS	6,074,000	4,827,000	10,901,000

(1) W. E. Morreson and C. L. Reading, "An Energy Model for the United States, Featuring Energy Balances for the Years 1947 to 1965 and Projections and Forecasts to the Year 1980 and 2000." IC 8384 - 1968. U.S. Dept. of Int. Bu. of Mines.

(2) R. L. Duprey, "Compilation of Air Pollutant Emission Factors," U.S. Dept. of H.E.W. P.H.S. Publ. No. 999-AP-42, 1968.

(3) Calculated on a BTU basis using a natural gas emission factor - i.e. (288/2850) x 160,000 = 16,000 Tons NO_x.

(4) Calculated as 3.7 lb. refuse per capita day (70% household and commercial -30% industrial).

(5) Assumed 20 lb. NO_x per Flight. Based on Estimate of Passenger-Miles. (Resources in America's Future)

(6) Weighted emission factor based on 71% household fuel and 29% commercial fuel used in 19 APC areas with 50,000,000 population.

(7) Composite emission factor calculated from Table 3-30.

(8) Pipeline = 601,000 tons NO_x; Gas Plant = 238,000 tons NO_x.

(9) Includes still gas used for fuel.

TABLE 3-24

ESTIMATED NO_x EMISSIONS FOR YEAR 1960

United States

Fuel Source	Household and Commercial	Industry Ex Pipeline and Gas Plant	Pipeline and Gas Plant(8)	Electric Generation	Total Stationary	Transportation	Grand Total
Natural Gas(1)-10^9 Ft^3 (10^{12} BTU)	4,123 (4,268)	5,381 (5,569)	680 (704)	1,724 (1,785)			
Tons $NO_x/10^9$ Ft^3	58(2)	121(7)	1,590(7)	195(2)			
Tons NO_x	239,000	652,000	1,081,000	336,000	2,308,000		2,308,000
Liquefied Gases(1)-10^6 BBl (10^{12} BTU)	101 (403)	142(9) (816)					
Tons $NO_x/10^6$ BBl							
Tons NO_x	23,000(3)	96,000(3)			119,000		119,000
Fuel Oil; Kerosene Distillate & Residual(1) 10^6 BBl (10^{12} BTU)	642 (3,785)	354		90 (564)		280 (1,693)	
Tons $NO_x/10^6$ BBl	617(6)	1,621(7)		2,184(2)		4,660(2)	
Tons NO_x	396,000	574,000		197,000	1,167,000	1,310,000	2,477,000
Coal + Lignite(1)-10^6 Tons (10^{12} BTU)	43 (1,168)	89 (2,644)		177 (4,257)		3 (91)	
Tons $NO_x/10^6$ Tons	4,000(2)	10,000(2)		10,000(2)		10,000	
Tons NO_x	172,000	890,000		1,770,000	2,832,000	30,000	2,862,000
Refuse Burning(4)-10^6 Tons	94	41					
Tons $NO_x/10^6$ Tons	738(2)	738(2)					
Tons NO_x	69,000	30,000			99,000		99,000
Gasoline(1)-10^6 BBl (10^{12} BTU)						1,519 (7,946)	
Tons $NO_x/10^6$ BBl						2,373(2)	
Tons NO_x						3,605,000	3,605,000
Jet Fuel(1)-10^6 BBl (10^{12} BTU)						136 (738)	
Tons $NO_x/10^6$ BBl							
Tons NO_x						9,000(5)	9,000
By-Product Fuels in Steel Industry		188,000			188,000		188,000
Total from Combustion-Tons NO_x	899,000	2,430,000	1,081,000	2,303,000	6,713,000	4,954,000	11,567,000
Non-Combustion Sources		119,000			119,000		119,000
				GRAND TOTALS	6,832,000	4,954,000	11,786,000

(1) W. E. Morrison and C. L. Readling, "An Energy Model for the United States, Featuring Energy Balances for the Years 1947 to 1965 and Projections and Forecasts to the Year 1980 and 2000." IC 8384 - 1968. U.S. Dept. of Int. Bu. of Mines.

(2) R. L. Duprey, "Compilation of Air Pollutant Emission Factors," U.S. Dept. of H.E.W. P.H.S. Publ. No. 999-AP-42, 1968.

(3) Calculated on a BTU basis using natural gas emission factor - i.e. (403/4268) x 239,000 = 22,600 tons.

(4) Calculated as 4 lb. refuse per capita day (70% household and commercial - 30% industrial).

(5) Assumed 20 lb. NO_x flight with 34.6 billion passenger miles (Resources in America's Future) and 37,000 estimated passenger miles per flight, results in 9,200 tons NO_x.

(6) Weighted emission factor based on 71% household fuel and 29% commercial fuel used in 19 APC areas with 50,000,000 population.

(7) Composite emission factor calculated from Table 3-30.

(8) Pipeline = 768,000 Tons NO_x; Gas Plant = 313,000 Tons NO_x.

(9) Includes still gas used for fuel.

TABLE 3-25

ESTIMATED NO_x EMISSIONS FOR YEAR 1965

United States

Fuel Source	Household and Commercial	Industry Ex Pipeline and Gas Plant	Pipeline and Gas Plant(8)	Electric Generation	Total Stationary	Transportation	Grand Total
Natural Gas(1)-10^9 Ft^3 (10^{12} BTU)	5,346 (5,534)	6,666 (6,899)	976 (1,010)	2,318 (2,399)			
Tons $NO_x/10^9$ Ft^3	58(2)	124(7)	1,995(7)	195(2)			
Tons NO_x	310,000	824,000	1,947,000	452,000	3,533,000		3,533,000
Liquefied Gases(1)-10^6 BBl (10^{12} BTU)	127 (511)	154(9) (888)					
Tons $NO_x/10^6$ BBl							
Tons NO_x	28,000(3)	106,000(3)			134,000		134,000
Fuel Oil: Kerosene Distillate & Residual(1) 10^6 BBl (10^{12} BTU)	716 (4,233)	395 (2,380)		119 (743)		304 (1,823)	
Tons $NO_x/10^6$ BBl	617(6)	1,605(7)		2,184(2)		4,660(2)	
Tons NO_x	442,000	634,000		260,000	1,336,000	1,417,000	2,753,000
Coal + Lignite(1)-10^6 Tons (10^{12} BTU)	22 (625)	98 (2,809)		245 (5,880)		7 (19)	
Tons $NO_x/10^6$ Tons	4,000(2)	10,000(2)		10,000(2)		10,000(2)	
Tons NO_x	88,000	980,000		2,450,000	3,518,000	7,000	3,525,000
Refuse Burning(4)-10^6 Tons	110	47					
Tons $NO_x/10^6$ Tons	738(2)	738(2)					
Tons NO_x	81,000	35,000			116,000		116,000
Gasoline(1)-10^6 BBl (10^{12} BTU)						1,750 (9,150)	
Tons $NO_x/10^6$ BBl						2,373(2)	
Tons NO_x						4,153,000	4,153,000
Jet Fuel(1)-10^6 BBl (10^{12} BTU)						221 (1,220)	
Tons $NO_x/10^6$ BBl						10,000(5)	10,000
Tons NO_x							
By-Product Fuel in Steel Industry		147,000			147,000		147,000
Total from Combustion - Tons NO_x	949,000	2,726,000	1,947,000	3,162,000	8,784,000	5,587,000	14,371,000
Non-Combustion Sources		17,4000			174,000		174,000
				GRAND TOTALS	8,958,000	5,587,000	14,545,000

(1) W. E. Morrison and C. L. Readling, "An Energy Model for the United States, Featuring Energy Balances for the Years 1947 to 1965 and Projections and Forecasts to the Year 1980 and 2000." IC 8384 - 1968. U.S. Dept. of Int. Bu. of Mines.

(2) R. L. Duprey, "Compilation of Air Pollutant Emission Factors," U.S. Dept. of H.E.W. P.H.S. Publ. No. 999-AP-42, 1968.

(3) Calc. from Natural Gas on a BTU Basis - i.e. (5/11/5534) x 310,000 = 28,500 Tons.

(4) Calculated as 4.4 lb. refuse per capita day (70% Household and Commercial - 30% Industrial).

(5) Assumed 20 lb. flight of Nox.". with 49 billion passenger miles (Resources in America's Future, Inc.) and 48,000 estimated passenger miles per flight. results in 10,260 tons NO_x for 1965.

(6) Weighted emission factor based on 71% household fuel and 29% commercial fuel used in 19 APC areas with 50,000,000 population.

(7) Composite Emission Factor calculated from Table

(8) Pipeline = 1,428,000 tons NO_x; Gas Plant = 519,000 tons NO_x.

(9) Includes still gas used for fuel.

TABLES 3-26

ESTIMATED POTENTIAL NO_x EMISSIONS FOR YEAR 1970

United States

Fuel Source	Household and Commercial	Industry Ex Pipeline and Gas Plant	Pipeline and Gas Plant $^{(6)}$	Electric Generation	Total Stationary	Transportation	Grand Total
Natural Gas$^{(1)}$-10^9 Ft^3 (10^{12} BTU)	6,504 (6,732)	7,583 (7,848)	1,190 (1,232)	2,610 (2,701)			
Tons $NO_x/10^9$ Ft^3	58$^{(2)}$	121$^{(3)}$	1,762$^{(3)}$	195$^{(2)}$			
Tons NO_x	377,000	917,000	2,097,000	509,000	3,900,000		3,900,000
Liquefied Gases$^{(1)}$-10^6 BBl (10^{12} BTU)	176 (706)	190$^{(4)}$ (1,045)					
Tons $NO_x/10^6$ BBl							
Tons NO_x	40,000$^{(5)}$	122,000$^{(5)}$			162,000		162,000
Fuel Oil: Kerosene Distillate & Residual$^{(1)}$ 10^6 BBl (10^{12} BTU)	693 (4,324)	445 (2,690)		152 (948)		382 (2,384)	
Tons $NO_x/10^6$ BBl	617$^{(2)}$	1,584$^{(2)}$		2,184$^{(2)}$		4,660$^{(2)}$	
Tons NO_x	428,000	705,000		332,000	1,465,000	1,780,000	3,245,000
Coal + Lignite$^{(1)}$-10^6 Tons (10^{12} BTU)	16 (416)	88 (2,510)		300 (7,200)			
Tons $NO_x/10^6$ Tons	4,000$^{(2)}$	10,000$^{(2)}$		10,000$^{(2)}$			
Tons NO_x	64,000	880,000		3,000,000	3,944,000		3,944,000
Refuse Burning$^{(1)}$-10^6 Tons	125	53					
Tons $NO_x/10^6$ Tons	738$^{(2)}$	738$^{(2)}$					
Tons NO_x	92,000	39,000			131,000		131,000
Gasoline$^{(1)}$-10^6 BBl (10^{12} BTU)						2,039 (10,644)	
Tons $NO_x/10^6$ BBl						2,373$^{(2)}$	
Tons NO_x						4,839,000	4,839,000
Jet Fuel$^{(1)}$-10^6 BBl (10^{12} BTU)						290 (1,604)	
Tons $NO_x/10^6$ BBl							
Tons NO_x						13,000	13,000
By-Product Fuel in Steel Industry		147,000			147,000		147,000
Total from Combustion - Tons NO_x	1,001,000	2,810,000	2,097,000	3,841,000	9,749,000	6,632,000	16,381,000
Non-Combustion Sources		235,000			235,000		235,000
				GRAND TOTALS	9,984,000	6,632,000	16,616,000

(1) Forecasts based on evaluations of historical growth rates and expected estimated technological and economic trends.

(2) Average emission factor assuming application of current (1968) controls.

(3) Composite Emission Factor calculated from Table 3-30.

(4) Includes still gas burned as fuel.

(5) Calculated on a BTU basis using natural gas emission factors.

(6) Pipeline = 1,553,000 tons NO_x; Gas Plant = 544,000 tons NO_x.

TABLE 3-27

ESTIMATED POTENTIAL NO$_x$ EMISSIONS FOR YEAR 1975

United States

Fuel Source	Household and Commercial	Industry Ex Pipeline and Gas Plant	Pipeline and Gas Plant(6)	Electric Generation	Total Stationary	Transportation	Grand Total
Natural Gas(1)-10^9 Ft^3 (10^{12} BTU)	7,913 (8,190)	8,632 (8,934)	1,440 (1,490)	2,938 (3,041)			
Tons NO$_x$/10^9 Ft^3	58(2)	119(3)	1,590(3)	195(2)			
Tons NO$_x$	459,000	1,025,000	2,289,000	573,000	4,346,000		4,346,000
Liquefied Gases(1)-10^6 BBl (10^{12} BTU)	245 (982)	232 (1,230)					
Tons NO$_x$/10^6 BBl							
Tons NO$_x$	56,000(5)	141,000(5)			197,000		197,000
Fuel Oil: Kerosene Distillate & Residual(1) 10^6 BBl (10^{12} BTU)	707 (4,412)	501 (3,020)		193 (1,210)		481 (3,001)	
Tons NO$_x$/10^6 BBl	617(2)	1,571(3)		2,184(2)		4,660	
Tons NO$_x$	436,000	787,000		423,000	1,646,000	2,241,000	3,887,000
Coal + Lignite(1)-10^6 Tons (10^{12} BTU)	13 (338)	79 (2,250)		366 (8,784)			
Tons NO$_x$/10^6 Tons	4,000(2)	10,000(2)		10,000(2)			
Tons NO$_x$	52,000	790,000		3,660,000	4,502,000		4,502,000
Refuse Burning(1)-10^6 Tons	142	61					
Tons NO$_x$/10^6 Tons	738(2)	738(2)					
Tons NO$_x$	105,000	45,000			150,000		150,000
Gasoline(1)-10^6 BBl (10^{12} BTU)						2,375 (12,398)	
Tons NO$_x$/10^6 BBl						2,373(2)	
Tons NO$_x$						5,636,000	5,636,000
Jet Fuel(1)-10^6 BBl (10^{12} BTU)						381 (2,107)	
Tons NO$_x$/10^6 BBl							
Tons NO$_x$						17,000	17,000
By-Product Fuels in Steel Industry		147,000			147,000		147,000
Total from Combustion - Tons NO$_x$	1,108,000	2,935,000	2,289,000	4,656,000	10,988,000	7,894,000	18,882,000
Non-Combustion Sources		318,000			318,000		318,000
				GRAND TOTALS	11,306,000	7,894,000	19,200,000

(1) Forecasts based on evaluation of historic growth rates and expected technological and economic trends.

(2) Estimated average emission factor assuming application of current (1968) controls.

(3) Composite Emission Factor calculated from Table 3-30.

(4) Includes still gas burned as fuel.

(5) Calculated on a BTU basis using natural gas emission factors.

(6) Pipeline = 1,711,000 tons NO$_x$; Gas Plant = 578,000 tons NO$_x$.

TABLE 3-28

ESTIMATED POTENTIAL NO_x EMISSIONS FOR YEAR 1980

United States

Fuel Source	Household and Commercial	Industry Ex Pipeline and Gas Plant	Pipeline and Gas Plant(6)	Electric Generation	Total Stationary	Transportation	Grand Total
Natural Gas(1)-10^9 Ft^3 (10^{12} BTU)	9,662 (10,000)	10,020 (10,371)	1,618 (1,675)	3,300 (3,451)			
Tons $NO_x/10^9$ Ft	58(2)	117(3)	1,526(3)	195(2)			
Tons NO_x	560,000	1,169,000	2,469,000	644,000	4,842,000		4,842,000
Liquefied Gases(1)-10^6 BBl (10^{12} BTU)	343 (1,405)	285(4) (1,444)					
Tons $NO_x/10^6$ BBl		163,000(5)					
Tons NO_x	79,000(5)				242,000		242,000
Fuel Oil: Kerosene Distillate & Residual(1) 10^6 BBl (10^{12} BTU)	679 (4,317)	563 (3,400)		250 (1,560)		607 (3,559)	
Tons $NO_x/10^6$ BBl	617(2)	1,558(3)		2,184(2)		4,660(2)	
Tons NO_x	419,000	877,000		546,000	1,842,000	2,820,000	4,662,000
Coal + Lignite(1)-10^6 Tons (10^{12} BTU)	10 (325)	71 (2,026)		445 (10,591)			
Tons $NO_x/10^6$ Tons	4,000(2)	10,000		10,000(2)			
Tons NO_x	40,000	710,000		4,450,000	5,200,000		5,200,000
Refuse Burning(1)-10^6 Tons	161	69					
Tons $NO_x/10^6$ Tons	738(2)	738(2)					
Tons NO_x	119,000	51,000			170,000		170,000
Gasoline(1)-10^6 BBl (10^{12} BTU)						2,761 (14,404)	
Tons $NO_x/10^6$ BBl						2,373(2)	
Tons NO_x						6,552,000	6,552,000
Jet Fuel(1)-10^6 BBl (10^{12} BTU)						502 (2,782)	
Tons $NO_x/10^6$ BBl							
Tons NO_x						23,000	23,000
By-Product Fuels in Steel Industry		147,000			147,000		147,000
Total from Combustion - Tons NO_x	1,217,000	3,117,000	2,469,000	5,640,000	12,443,000	9,395,000	21,838,000
Non-Combustion Sources		432,000			432,000		432,000
				GRAND TOTAL	12,875,000	9,395,000	22,278,000

(1) Forecasts based on evaluation of historical growth rates and expected technological and economic trends.

(2) Estimated average emission rates assuming application of current (1968) controls.

(3) Composite Emission Factor calculated from Table I.

(4) Includes still gas burned as fuel.

(5) Calculated on a BTU basis using natural gas emission factors.

(6) Pipeline = 1,860,000 tons NO_x; Gas Plant = 609,000 tons NO_x.

(7) Calculated as 5.5 pounds refuse per capita day (70% household and commercial; 30% industrial).

TABLE 3-29

ESTIMATED POTENTIAL NO_x EMISSIONS FOR YEAR 2000

United States

Fuel Source	Household and Commercial	Industry Ex Pipeline and Gas Plant	Pipeline and Gas Plant(4)	Electric Generation	Total Stationary	Transportation	Grand Total
Natural Gas(1)-10^9 Ft^3 (10^{12} BTU)	18,475 (19,066)	16,211 (16,778)	1,720 (1,780)	4,240 (4,370)			
Tons $NO_x/10^9$ Ft^3	58(2)	112(3)		195(2)			
Tons NO_x	1,072,000	1,820,000	2,626,000	827,000	6,345,000		6,345,000
Coal and Lignite(1)-10^6 Tons (10^{12} BTU)		76 (2,169)		1,120 (26,900)			
Tons $NO_x/10^6$ Tons		10,000(2)		10,000(2)			
Tons NO_x		760,000		11,200,000	11,960,000		11,960,000
Petroleum(1)(6)-10^6 BBl (10^{12} BTU)	318 (2,000)	548 (3,441)		370 (2,330)		6,627 (41,648)	
Tons $NO_x/10^6$ BBl	617(2)	1,536(3)		2,184(2)		2,790(2)	
Tons NO_x	196,000	842,000		808,000	1,846,000	18,488,000	20,334,000
Refuse Burning(5)-10^6 Tons	249	108					
Tons $NO_x/10^6$ Tons	738(2)	738(2)					
Tons NO_x	184,000	80,000			264,000		264,000
Tons NO_x from Combustion	1,452,000	3,502,000	2,626,000	12,835,000	20,415,000	18,488,000	38,903,000
Non-Combustion Sources		1,140,000			1,140,000		1,140,000
				GRAND TOTALS	21,555,000	18,488,000	40,043,000

(1) Forecasts based on evaluation of historical growth rates and expected technological and economic trends.

(2) Extimated average emission factors assuming application of current (1968) controls.

(3) Composite emission rate calculated from Table 3-30.

(4) Pipeline = 766,000 tons NO_x; Gas Plant = 660,000 tons NO_x.

(5) Calculated as 6.8 pounds refuse per capita day (70% household and commercial; 30% industrial).

(6) Includes natural gas liquids.

Tables 3-22 through 3-29 indicate that NO_x emissions from all major sources amounted to about 9.4 million tons in 1950, 11 million tons in 1955, 12 million tons in 1960 and 15 million tons in 1965. The projected figures based on extrapolation of current economic and technological trends are 17 million tons in 1970, 19 million in 1975, 22 million in 1980 and 40 million tons in the year 2000. Stationary sources account for about 55 to 60% of the emissions and mobile sources about 40 to 45% for the period 1950 through 1980. The electric generation sector accounts for an estimated 25% of the stationary sources in 1950. However, because of its rapid growth, electric generation continuously increases as a proportion of the stationary sources to 34% in 1960, 35% in 1965, 38% in 1970, 43% in 1975, 44% in 1980 and 60% in the year 2000. It has been assumed in these calculations that hydropower plus nuclear power account for about 17% of the gross energy input to electricity generating ultilities in 1965, 29% in 1980 and 60% in the year 2000.

Basic data and projections for NO_x emissions from the oil and gas industries, as discussed in Section 3.1.2 are summarized in Table 3-30.

Tables similar to Tables 3-22 through 3-29 have been calculated for each of the 50 United States for the years 1960 and 1965. These emissions have been analyzed in some detail by regression models in order to establish a firm basis for projection purposes. Preliminary studies show that for the year 1960, 90% of the variation in total NO_x emissions for combustion for the 50 states is explained by or related to total State population. It was also found that car registrations explain about 90% of the variations in NO_x emissions for transportation. Regional considerations have been incorporated into the cost effectiveness analysis of NO_x control methods discussed in Section 9.

Figure 3-14 presents the data from Tables 3-22-29 for ready visual analysis. The total potential emissions based on median economic trends for stationary and mobile sources increase rapidly from 9 million tons in 1950 to about 40 million tons in 2000. The household and commercial sector accounts for a continuously decreasing percentage of the total, i.e., from 9% in 1950 to 6% in 1980 to 4% in the year 2000. Some factors contributing to this rapid decrease are the relatively low projected growth rates for population (1.2% per year) and household formation (1.4 to 2% per year) compared to the growth rate of other major sectors (3 to 9%), the substitution of oil and gas for coal, and the increasing use of electricity.

Industrial (ex pipelines and gas plants) sources also account for a decreasing percentage of the total potential NO_x emission. From 25% in 1950, industrial sources are estimated to decline to 20% in 1965, and are projected to decline to 16% in 1980, to about 11% in the year 2000. From 1950 to the present, coal has been losing market position in industry to oil and gas, while demand for electricity has been growing rapidly. These trends are expected to continue into the near future. The lower NO_x emission factors for industrial use of gas (205 pounds NO_x per 10^9 BTU, compared to 480 lb. and 842 lb. NO_x per 10^9 BTU, respectively, for fuel oil and coal) exert a multiplying effect on these trends.

Potential NO_x emissions from the electric utility sector have increased rapidly as the demand for electricity has about doubled in each past ten year period. From an estimated 14% of total emissions in 1950, utilities are estimated to increase their NO_x emissions to 22% in 1965, 25% in 1980 and 32% in the year 2000. The projected demand

TABLE 3-30

Potential NO_x Emissions from Oil and Gas Industries

	1950	1955	1960	1965	1970	1975	1980	2000
Pipeline								
Fuel Use - 10^9 cu ft								
Gas Engines	190	240	305	388	420	460	500	520
Gas Turbines	0	5	45	124	200	320	345	680
								1,200
Emission Factors - lbs/10^3 ft^3								
Gas Engines	5.0	5.0	5.0	7.3	7.3	7.3	7.3	7.3
Gas Turbines	--	0.2	0.2	0.2	0.2	0.2	0.2	0.2
NO_x, 10^3 Tons/yr								
Gas Engines	475	600	763	1,416	1,533	1,679	1,825	1,898
Gas Turbines	--	1	5	12	20	32	35	68
Total	475	601	768	1,428	1,553	1,711	1,860	1,966
Gas Plant								
Fuel Use - 10^9 cu ft								
Gas Engines	99	130	170	231	238	250	260	270
Gas Turbines	0	0	3	13	82	120	177	310
Gas Furnace	91	110	157	220	250	290	336	520
Emission Factors - lbs 10^3 ft^3								
Gas Engines	3.5	3.5	3.5	4.3	4.3	4.3	4.3	4.3
Gas Turbines	--	--	0.2	0.2	0.2	0.2	0.2	0.2
Gas Furnace	0.19	0.19	0.19	0.19	0.19	0.19	0.19	0.19
NO_x - 10^3 Tons/yr								
Gas Engines	173	228	298	497	512	538	559	580
Gas Turbines	--	--	--	1	8	12	18	31
Gas Furnace	9	10	15	21	24	28	32	49
Total	182	238	313	519	544	578	609	660
Refining								
Gas, Total, 10^9 cu ft								
Gas Engines	39	39	39	39	40	40	40	40
Turbines	0	0	21	52	58	66	74	160
Furnaces	991	1,161	1,340	1,609	1,802	1,894	1,930	2,300
Oil Furnaces - 10^6 bbl	52	48	44	40	37	33	30	20
Emission Factors								
Gas Engines - lbs/10^3 ft^3	2.0	2.0	2.0	4.35	4.35	4.35	4.35	4.35
Turbines - lbs/10^3 ft^3	--	--	0.2	0.2	0.2	0.2	0.2	0.2
Furnaces - lbs/10^3 ft^3	0.21	0.21	0.21	0.21	0.21	0.21	0.21	0.21
Oil Furnaces - lbs/bbl	1.624	1.624	1.624	1.624	1.624	1.624	1.624	1.624
NO_x - 10^3 Tons/yr								
Gas Engines	39	39	39	85	87	87	87	87
Turbines	--	--	2	5	6	7	7	16
Furnaces	104	122	141	169	189	199	203	246
Oil Furnaces	84	78	71	65	60	54	49	32
Total NO_x Emissions	227	239	253	324	342	347	346	377

TABLE 3-30 (Continued)

	1950	1955	1960	1965	1970	1975	1980	2000
Producing								
Gas - 10^9 cu ft								
Gas to Heaters and Boilers	880	800	640	544	440	360	288	170
Gas to Engine	220	205	175	136	110	90	72	30
Oil to Diesel - 10^6 bbl	13	12	11	10	9	8	7	4
Emission Factors***								
Gas to Heaters - lbs/10^3 ft^3	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2
Gas to Engine - lbs/10^3 ft^3	0.77	0.77	0.77	0.77	0.77	0.77	0.77	0.77
Oil to Diesel - lbs/bbl	4.65	4.65	4.65	4.65	4.65	4.65	4.65	4.64
NO_x, 10^3 Tons/yr								
Gas to Heaters and Boilers	88	80	64	54	44	36	29	17
Gas to Engine	85	79	67	52	42	35	28	12
Oil to Diesel	60	56	51	47	42	37	33	18
Total	233	214	182	153	143	135	131	47
Gas Total Industry - 10^9 ft^3	3,317	4,680	6,061	7.642	8,773	10.073	11,638	17,931
Pipeline - Gas Vol 10^9 ft^3	190	245	350	512	620	780	845	1,200
Em. Factor - Tons/10^6 ft^3	2.5*	2,45*	2.19*	2.79*	2.50*	2.20*	2.20*	1.64*
Tons NO_x	475,000	601,000	768,000	1,428,000	1,553,000	1,711,000	1,860,000	1,966,000
Gas Plants - 10^9 ft^3	190	240	330	464	570	660	773	520
Em. Factor - Tons/10^6 ft^3	0.958	0.992	0.948	1.12	0.954	0.876	0.788	1.27
NO_x Emissions - Tons	182,000	238,000	313,000	519,000	544.000	478,000	609,000	660,000
Prod. & Refining - 10^9 ft^3	2,130	2,205	2,216	2,380	2,450	2,450	2,404	2,700
NO_x Emissions - Tons	316,000	320,000	313,000	365,000	368,000	364,000	354,000	374,000
Gas - Ind. Ex Pipeline and Gas Plant	2,937	4,195	5,381	6,666	7,583	8,632	10,020	16,211
Composite E.F. - Tons/10^9 ft^3*	165	127	121	124	121	119	117	112
NO_x Emissions - Tons	402,000	533,000	652,000	824,000	917,000	1,025,000	1,169,000	1,820,000
Gas - Ind. Ex (P + G.P.) Less (P&R)	807	1,990	3,165	4,286	5,133	6,182	7,616	13,511
Em. Factor** - Tons/10^6 ft^3	.107	.107	.107	.107	.107	.107	.107	.107
NO_x Emissions - Tons	86,000	213,000	339,000	459,000	549,000	661,000	815,000	1,446,000
Oil - Total Industry - 10^6 bbl	301	348	354	395	445	501	563	548
Oil (Prod. and Ref.)	-65	60	55	50	46	41	37	24
Net Oil	236	288	299	345	399	460	526	524
E. Factor** - Tons/10^6 bbl	1,512	1,512	1,512	1,512	1,512	1,512	1,512	1,512
NO_x Emissions - Tons	357,000	435,000	452,000	522,000	603,000	696,000	795,000	792,000
Plus NO_x Free Prod. and Ref. - Tons	144,000	134,000	122,000	112,000	102,000	91,000	82,000	50,000
Total NO_x - Tons	501,000	569,000	574,000	634,000	705,000	787,000	877,000	842,000
Composite E.F. - Tons/10^6 bbl	1,664	1,635	1,621	1,605	1,584	1,571	1,558	1,536

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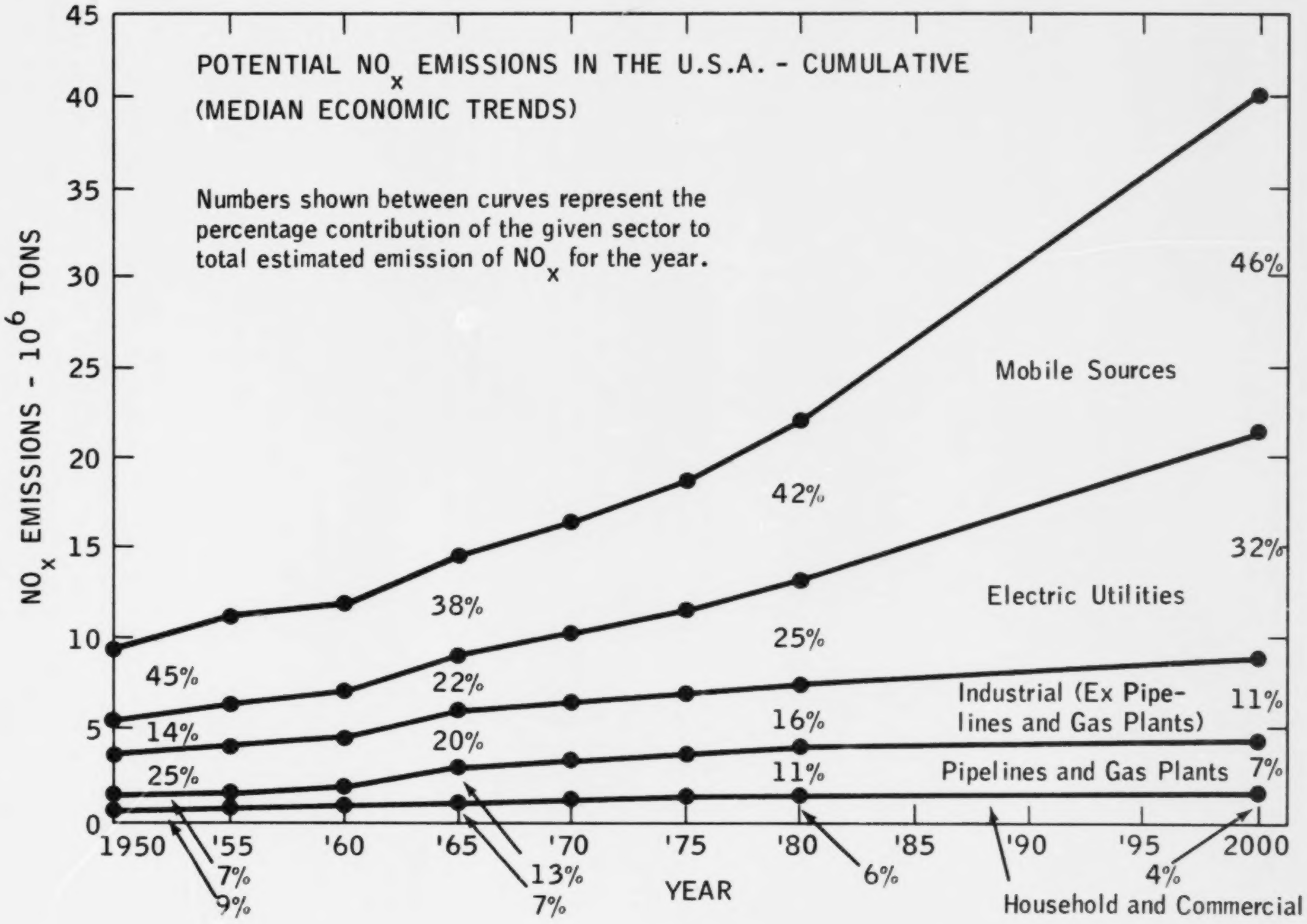
* Composite emission factor.

** Duprey, R. L. -"Compilation of Emission Factors," U.S. Department of Health, Education and Welfare, P.H.S. Publ. No. 999, AP-42, 1968.

*** Em. Factor; E.F. = Emission Factor.

Figure 3-14


POTENTIAL NO_x EMISSIONS IN THE U.S.A. - CUMULATIVE
(MEDIAN ECONOMIC TRENDS)
Numbers shown between curves represent the percentage contribution of the given sector to total estimated emission of NO_x for the year.
NO_x EMISSIONS - 10^6 TONS
45
40
35
30
25
20
15
10
5
0
1950
'55
'60
'65
'70
'75
'80
'85
'90
'95
2000
YEAR
Mobile Sources
Electric Utilities
Industrial (Ex Pipelines and Gas Plants)
Pipelines and Gas Plants
Household and Commercial
45%
14%
25%
7%
9%
38%
22%
20%
13%
7%
42%
25%
16%
11%
6%
46%
32%
11%
7%
4%

for electricity is expected to continue at approximately its present growth rate of 6 to 7% per year. However, the rapid projected growth of nuclear power over fossil fuel will begin to slow the rate of increase of NO_x emissions from this sector. Our electric power estimates are based on nuclear generating capacity of 110,000 megawatts in 1980 and 790,000 megawatts in the year 2000 as shown below:

Table 3-31

Electricity Capacity and Generation

Year	1965		1980		2000	
	Capacity (1000 MW)	Gen. (10^9 KWH)	Capacity (1000 MW)	Gen. (10^9 KWH)	Capacity (1000 MW)	Gen. (10^9 KWH)
Fossil	191	857	360	1770	766	3970
Nuclear	1	4	110	720	790	5530
Hydro	44	194	75	320	100	500
TOTAL	236	1055	545	2810	1656	10,000

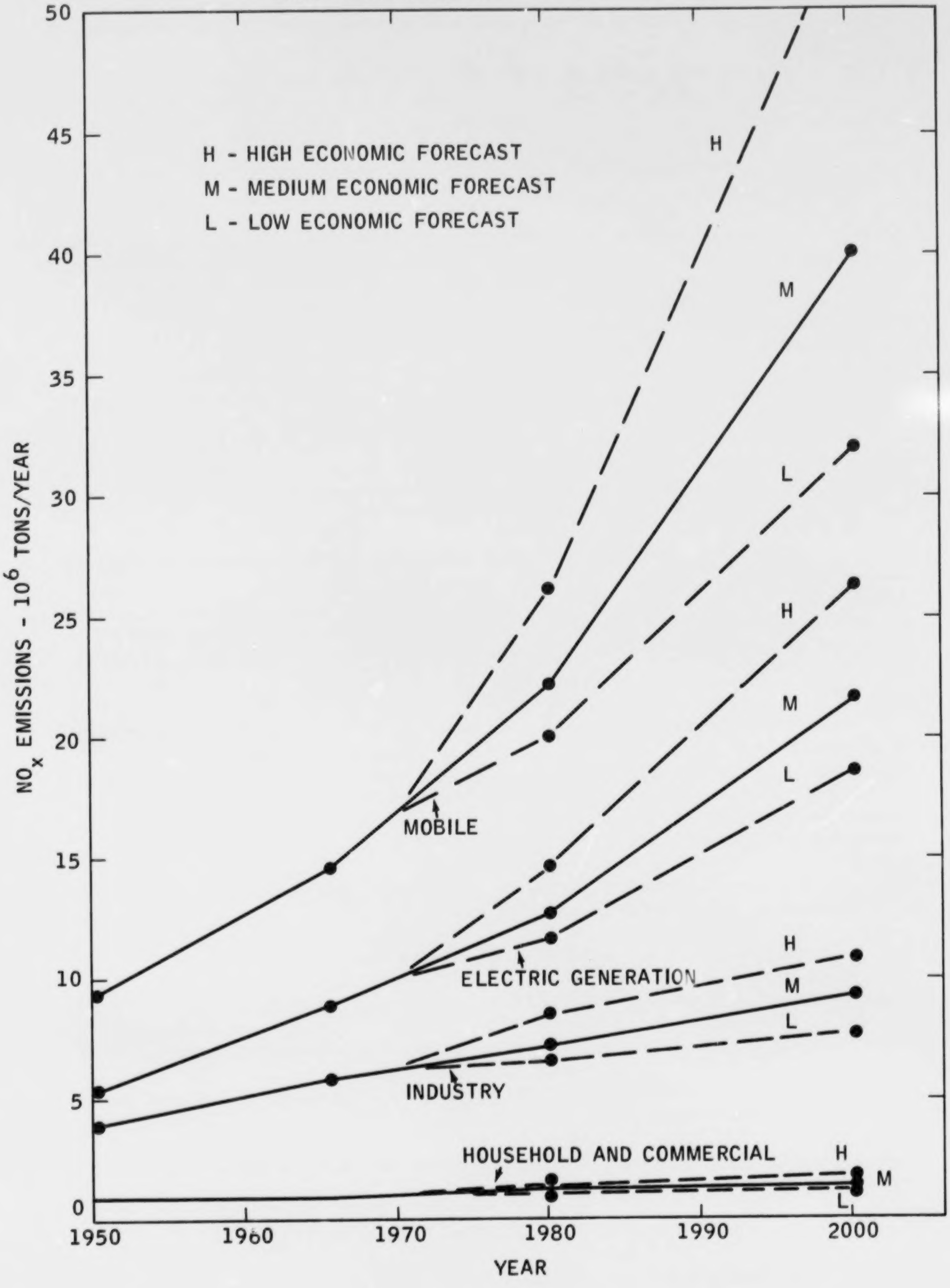
Non-combustion sources, chiefly nitric acid manufacture and uses, represent a small but growing percentage of estimated total NO_x emissions. Mobile sources (autos, trucks, buses, diesel locomotives, inland waterways, airplanes) account for almost one-half of the total potential NO_x emissions. Assuming no NO_x emission control or major technological changes, the mobile sector would increase its share of potential NO_x emission to the year 2000. These assumptions are, of course, highly suspect in view of the wide general interest in reducing air pollution and the magnitude of research effort aimed at NO_x control on conventional engines, and possible development of commercially viable steam cars, electric cars, fuel cell-powered vehicles etc. This systems study has not concerned itself in depth with mobile sources. These rough estimates are included simply to indicate the relative importance of stationary sources to the total potential NO_x emissions.

3.4. POTENTIAL EFFECT OF ECONOMIC TRENDS, TECHNOLOGICAL CHANGES AND NO_x CONTROLS ON EMISSIONS

Figure 3-15 gives estimates of potential NO_x emissions (assuming minimum controls) based on fuel consumption for low, medium and high economic activity. Our model for the medium forecast is based on a 4% average annual rate of growth for real GNP, a 1.2% population growth and a "composite" index of industrial production growth rate of 4.4%. The low and high forecasts are based on GNP growth rates of 3 and 5%, population growth rates of 1.0% and 1.6% and industrial production at 4% and 6% growth rates. The low, medium and high growth rates for electric generation, number of households and mobile consumption are based upon analyses of past trends and comparison with a number of private and published forecasts, including "The Year 2000" (3-98) "Resources in America's Future " (3-99) and "Energy in the United States." (3-100).

Figure 3-15

POTENTIAL NO_x EMISSIONS 10^6 TONS/YEAR
LOW, MEDIUM AND HIGH ECONOMIC FORECASTS



These ranges of forecasts indicate potential NO_x emissions under different broad economic assumptions, with continuation of evolutionary technological advances and the use of current limited NO_x control technology.

Figure 3-16 provides a breakdown of stationary sources of potential NO_x emissions by type of fuel and consumption sector based on medium economic projections and conventional technology. The trends previously described are readily apparent. Emissions from coal burned in electric generation and gas burned in industry would account for the bulk of emissions in the year 2000.

Although Figure 3-15 indicates that NO_x emission projections have a wide range of uncertainty due to changes in general economic assumptions, major technology breakthroughs could have an additional significant effect on energy use and therefore, potential NO_x emissions. Figure 3-17 indicates the basis selected for evaluating the effect of some breakthrough technological alternatives for the year 2000. The potential NO_x emissions (10^6 tons) from stationary and mobile sources for the years 1965, 1980, and 2000 are the median projections shown on Figure 3-15. The shaded areas at the top of each bar indicate the potential NO_x emissions saved through use of hydro and nuclear electric generation. Thus, potential stationary NO_x emissions would have increased by 8% in 1965, to an estimated 26% increase in 1980 and 90% in the year 2000, if projected electric power demands were met by conventional fossil fuel steam boilers only.

The projected growth of NO_x emissions by conventional technology between the years 1980 and 2000 are shown as Δ stationary, Δ mobile and Δ hydro and nuclear power. These "deltas" denote changes in the magnitude of NO_x emissions based on advanced technology assumed replacing 1980 conventional technology in our technological breakthrough analysis, as shown in Table 3-32.

Morphological analysis is useful in indicating the extreme range of NO_x emissions that might result from alternative energy uses in the relatively distant future. To perform this analysis, all combinations of 6 Electric Generation Alternatives, 4 Transportation lternatives and 3 Industrial, Household and Commercial Alternatives have been calculated. The electric generation alternatives are:

U-1. Conventional steam boilers fired with oil, gas and coal; hydrogeneration and nuclear generation.

U-2. Conventional steam boilers fired with natural gas only.

U-3. Conventional steam boilers fired with bituminous coal only.

U-4. Conventional steam boilers fired with residual fuel oil only.

U-5. Conventional steam boilers fired only with present-type water cooled, nuclear reactors.

U-6. Electricity generated from hydrocarbon-air fuel cells using natural gas as source fuel.

The four transportation alternatives are:

T-1. Conventional auto and trucks

Figure 3-16

ESTIMATED AND POTENTIAL NO_x EMISSIONS SPLIT BY FUEL AND SECTOR - STATIONARY SOURCES

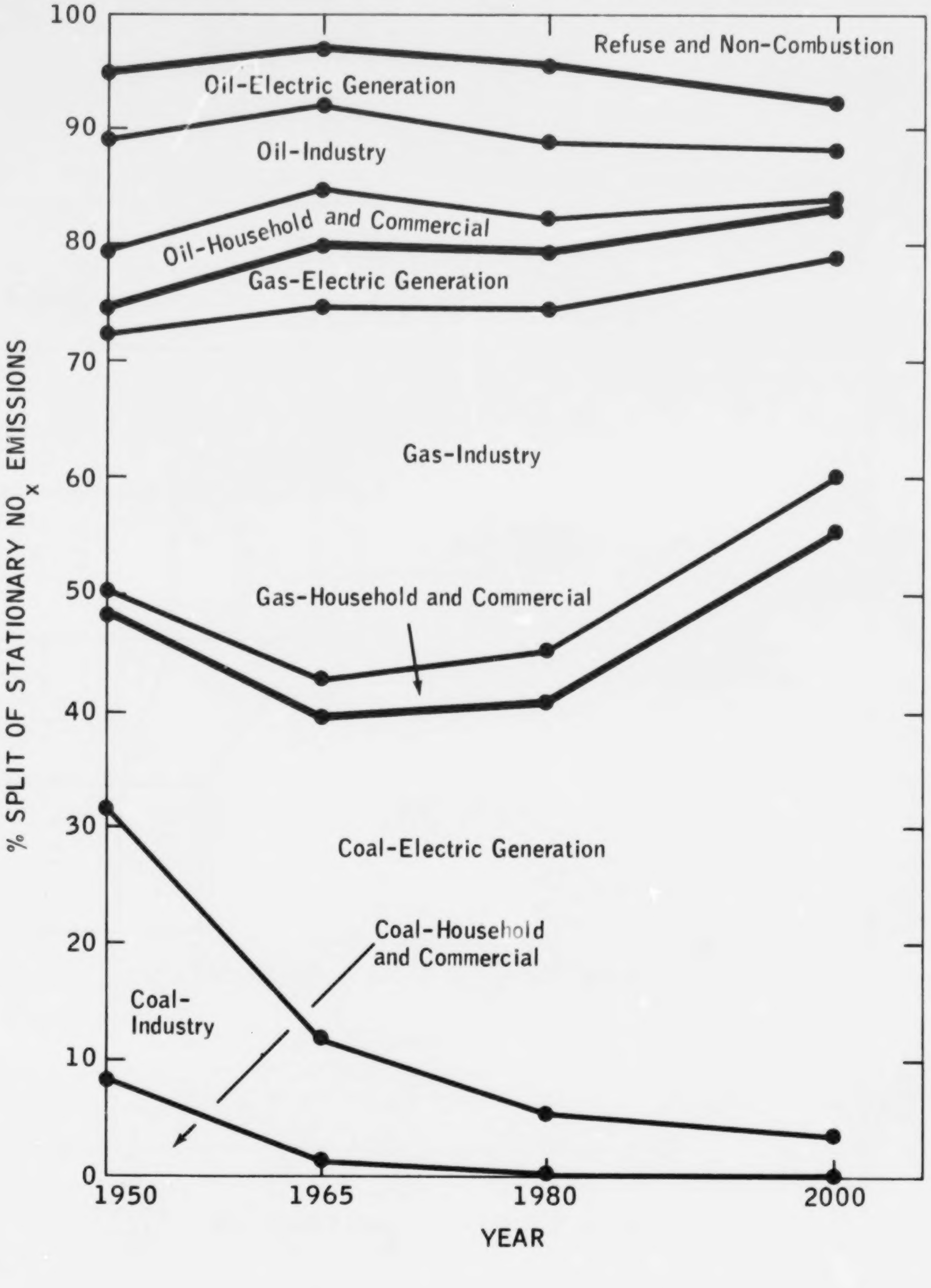


Figure 3-17

POTENTIAL NO_x EMISSIONS -
BASES FOR TECHNOLOGICAL BREAKTHROUGH ALTERNATIVES

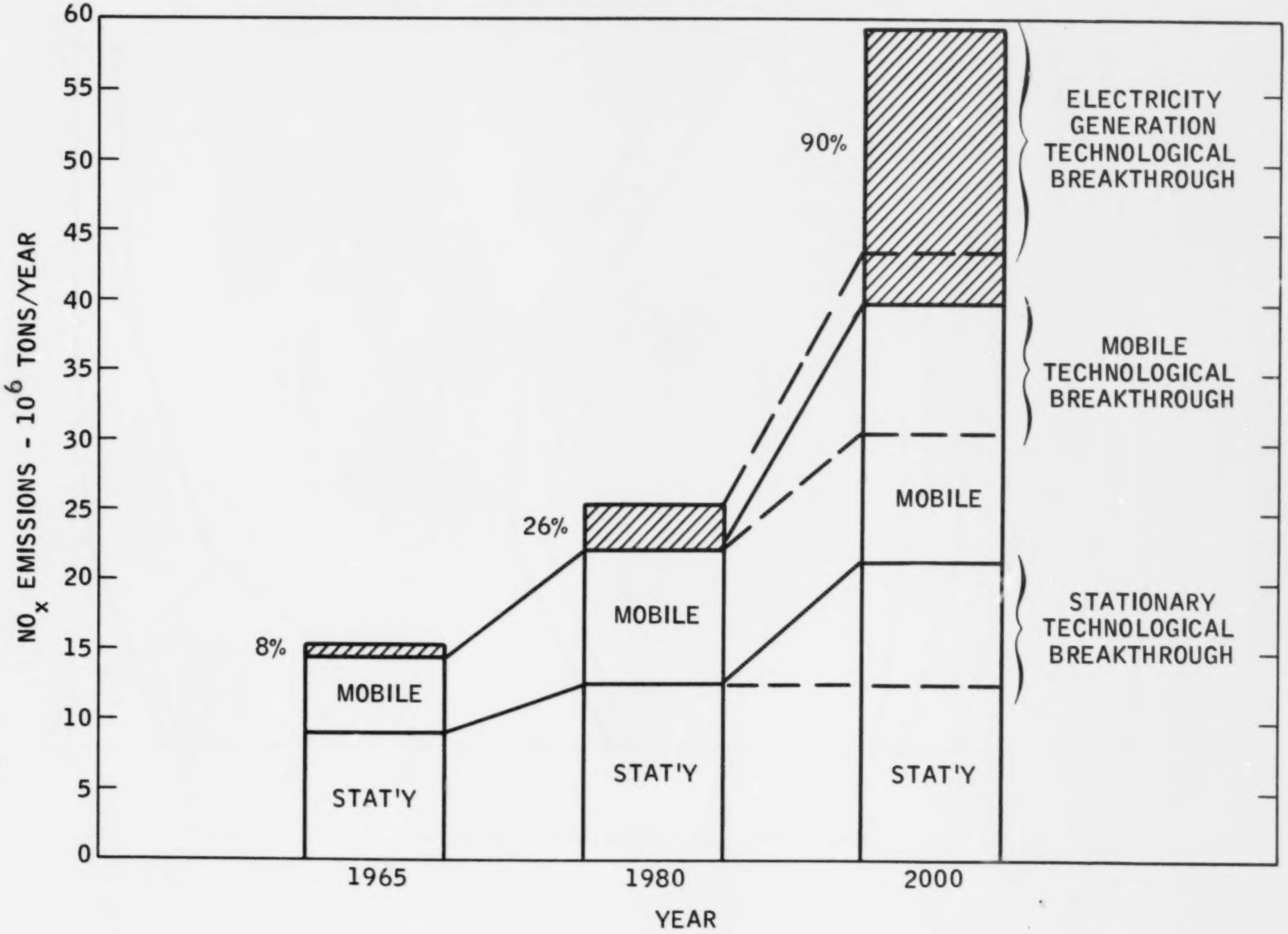


TABLE 3-32

YEAR 2000 POTENTIAL NO_x EMISSIONS -10^6 TONS - TECHNOLOGICAL ALTERNATIVES

		I-1 Conventional				I-2 △ by Fuel Cells				I-3 △ by Electricity			
		T-1 Conv.(a)	T-2 El. Car(b)	T-3 F. Cell(c)	T-4 St. Car(d)	T-1 Conv.(a)	T-2 El. Car(b)	T-3 F. Cell(c)	T-4 St. Car(d)	T-1 Conv.(a)	T-2 El. Car(b)	T-3 F. Cell(c)	T-4 St. Car(d)
U-1 Conventional	Stationary	21.5	26.4	21.5	21.5	12.9	15.7	12.9	12.9	25.9	30.2	25.9	25.9
	Mobile	18.5	9.4	9.4	11.7	18.5	9.4	9.4	11.7	18.5	9.4	9.4	11.7
	Total	40.0	35.8	30.9	33.2	31.4	20.1	22.3	24.6	44.4	39.6	35.3	37.6
U-2 Conventional △ by Gas	Stationary	26.3	32.5	26.3	26.3	12.9	19.2	12.9	12.9	32.8	37.6	32.8	32.8
	Mobile	18.5	9.4	9.4	11.7	18.5	9.4	9.4	11.7	18.5	9.4	9.4	11.7
	Total	44.8	41.9	35.7	38.0	31.4	28.6	22.3	24.6	51.3	47.0	42.2	44.5
U-3 Conventional △ by Coal	Stationary	39.4	52.5	39.4	39.4	12.9	26.0	12.9	12.9	54.0	61.7	54.0	54.0
	Mobile	18.5	9.4	9.4	11.7	18.5	9.4	9.4	11.7	18.5	9.4	9.4	11.7
	Total	57.9	61.9	48.8	51.1	31.4	35.4	22.3	24.6	72.5	71.1	63.4	65.7
U-4 Conventional △ by Oil	Stationary	37.0	49.0	37.0	37.0	12.9	24.8	12.9	12.9	49.4	57.1	49.4	49.4
	Mobile	18.5	9.4	9.4	11.7	18.5	9.4	9.4	11.7	18.5	9.4	9.4	11.7
	Total	55.5	58.4	46.4	48.7	31.4	34.2	22.3	24.6	67.9	66.5	58.8	61.1
U-5 Conventional △ by Nuclear	Stationary	14.4	14.4	14.4	14.4	12.9	12.9	12.9	12.9	12.9	12.9	12.9	12.9
	Mobile	18.5	9.4	9.4	11.7	18.5	9.4	9.4	11.7	18.5	9.4	9.4	11.7
	Total	32.9	23.8	23.8	26.1	31.4	22.3	22.3	24.6	31.4	22.3	22.3	24.6
U-6 Conventional △ by Fuel Cell	Stationary	14.4	14.4	14.4	14.4	12.9	12.9	12.9	12.9	12.9	12.9	12.9	12.9
	Mobile	18.5	9.4	9.4	11.7	18.5	9.4	9.4	11.7	18.5	9.4	9.4	11.7
	Total	32.9	23.8	23.8	26.1	31.4	22.3	22.3	24.6	31.4	22.3	22.3	24.3

(a) Conventional
(b) Electric Car
(c) Fuel Cell
(d) Steam Car

T-2. Electric auto-using utility electricity with an average efficiency of 42%.

T-3. Hydrocarbon-air fuel cell powered vehicles.

T-4. Steam cars

The three industrial, household and commercial alternatives are:

I-1. Conventional combustion processes using all fossil fuels.

I-2. Fuel cell fired with natural gas.

I-3. All electric-utility generated.

The results of this analysis are shown in Table 3-32 for the year 2000. The data in the body of the tables are estimated United States NO_x emissions in millions of tons from stationary sources, transportation sources and total stationary plus transportation sources. These results were calculated using current emission factors and assuming no NO_x emission controls.

Examining Table 3-32, we see that for the base case I-1/T-1/U-1 (all sectors using conventional combustion technology), the estimated uncontrolled NO_x emissions would be 21.5 million tons from stationary sources and 18.5 million tons from transportation sources for a total of 40 million tons. However, if we assume that Δ transportation consists of electric vehicles (T-2) powered by batteries charged from conventional utility (U-1) electricity, total NO_x emissions would decrease to 35.8 million tons. In this case, (I-1/T-2/U-1), increased NO_x emissions from utilities would be more than offset by the decrease of transportation NO_x emissions. Proceeding to case I-1/T-3/U-1 where Δ transportation is assumed to be powered by non-NO_x emitting fuel cells, the total emissions are estimated to be 30.9 million tons or about 77% of the base case I-1/T-1/U-1. Case I-1/T-1/U-2 produces higher emissions than the base case (I-1/T-1/U-1) since it is assumed that there is no Δ hydro or nuclear generated electricity in U-2. The effect of fueling (the Δ utilities) growth with a single fuel, coal (U-3) or fuel oil (U-4) compared with natural gas (U-2), results in total NO_x emissions of 57.9 million tons for coal, 55.5 for fuel oil vs. 44.8 using natural gas.

These 72 alternate cases present a wide range of possible NO_x emissions based on possible fuel substitution and/or technological breakthroughs for the year 2000. There are a number of cases that would result in a low NO_x emission rate of 22.3 million tons, while the maximum NO_x emission of 72.5 million tons would result from case I-3/U-3/T-1 (Δ Industrial growth by electric heat and power, Δ transportation by conventional car and Δ power generation by coal only.)

It is difficult, at this time, to provide precise probabilities for the occurrence of each of these technological alternatives for the year 2000. However, a few tentative statements should be made. The possibility of an economically feasible steam car seemed reasonable to many people in the recent past. However, William Lear's very pessimistic appraisal (3-101) of the future of the steam automobile afer spending $5.5 million in the effort casts considerable doubt on any significant possibility for mass produced steam cars. Similarly, the wide-spread use of fuel cell or fuel cell/battery hybrid-power sources is considered unlikely for general purpose automobiles. Thus, conventional transportation should be given the highest probabilities.

Other spokesmen, such as G. C. Gambs, Manager of Planning and Development of Gibbs & Hill, Inc., have forecast (3-17) that coal used for power generation will decrease to 226 million tons in 1990 from 307 million tons in 1970 with nuclear generation taking up most of the slack. Mr. Gambs cites the fact that the coal industry is a "labor intensive industry while the nuclear industry is not." Recent costly mine safety rulings, slow-down of production rates, and relative economics are also cited to support these forecasts. On the other hand, recent late completion of nuclear generation plants due to production and fabrication problems; potential thermal pollution; additional safety regulations; limited approved site locations; etc., are reasons given for not meeting optimistic nuclear generation forecasts.

For these and other reasons, attempts have not been made to place quantitative probabilities on the year 2000 technological alternatives. Aiming the proposed research and development projects at the nearer and clearer goal of 1980, where technological advances will be less extreme and the NO_x problem can be better defined, is a practical approach. However, it is recommended that periodical reviews be made of the impact that actual technological breakthroughs will have on the NO_x problem, so that research and development efforts will be most useful.

3.5. SUMMARY

In this section we have characterized the problem of NO_x emissions for stationary sources into broad fuel consumption sections by fuel type for the period of 1950 with forecasts to the year 2000. The changes in the magnitude of the problem due to varying economics, technological and socio-political assumptions have also been indicated. To put the primary individual sources of NO_x emissions into proper perspective, we show a summary for the year 1980 in Table 3-33 below.

Table 3-33

Potential Emissions From Major Sources - Year 1980

Major Source	Potential Emissions (Uncontrolled) 10^6 Tons	% of Total
1. Power Plants:	8.8	55
Coal 5.6 Gas 2.3 Oil 0.9		
2. Pipeline Engines	1.8	11
3. Industrial Boilers	1.5	9
4. Gas Plant Piston Engines:	.6	4
• Less than 300 HP-.02 • 300-1800 HP-.33 • 1800 + HP-.21		
5. Nitric Acid Plants:	.3	2
Old .16 New .13		
6. Refinery Sources:	.3	2
Furnaces .20 I.C. Engines .09		
	13.3	83
7. All Other Sources:	2.8	17
Household & Comm. 1.2 Other Ind. 1.5		
Total Stationary	16.1	100

These forecasts have been compared with a number of published (3-12), and (3-98) through (3-107) and private sources in developing our final forecasts. Table 3-34 below, summarizes NO_x emissions in millions of tons from Tables 3-22 to 3-29 by major sectors.

Table 3-34

U.S. NO_x Emissions Assuming Minimum Controls(1)
(10^6 Tons and % of Total Stationary Emissions)

Year	Household and Commercial	Industrial Ex Pipeline & Gas Plants	Pipelines & Gas Plants	Electric Generation	Total Stationary	Mobile	Grand Total
1950	0.86 17%	2.38 46%	0.66 13%	1.28 25%	5.2 100%	4.2	9.4
1955	0.84 14%	2.55 42%	0.84 14%	1.84 30%	6.1 100%	4.8	10.9
1960	0.90 13%	2.55 37%	1.08 16%	2.30 34%	6.8 100%	5.0	11.8
1965	0.94 11%	2.90 32%	1.95 22%	3.16 35%	9.0 100%	5.6	14.6
1970	1.00 10%	3.05 30%	2.10 21%	3.84 39%	10.0 100%	6.3	16.6
1975	1.11 10%	3.25 29%	2.29 20%	4.66 42%	11.2 100%	7.9	19.1
1980	1.22 9%	3.55 28%	2.47 19%	5.64 44%	12.9 100%	9.4	22.3
2000	1.45 7%	4.64 21%	2.63 12%	12.84 60%	21.6 100%	18.5	40.04

(1) Individual emission factors, fuel usage, and annual emission are presented in detail for the years 1950-2000 in Tables 3-22 through 3-29.

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4. CONTROL OF NO_x EMISSIONS BY COMBUSTION MODIFICATION

Oxides of nitrogen are produced in all fossil fuel combustion processes with air as the oxidant. At flame temperatures, the direct combination of atmospheric nitrogen and oxygen results in the formation of nitric oxide. Although nitric oxide becomes thermodynamically unstable as heat is removed from the combustion gases and the temperature drops to lower levels, its decomposition is kinetically limited and the nitric oxide concentration remains frozen below about 2300-2400°F. Subsequently, at lower temperatures, a small fraction of the nitric oxide produced may be oxidized by the excess oxygen in the combustion equipment to nitrogen dioxide. As will be discussed, the latter process is favored both by equilibrium and kinetic rates with decreasing temperatures. However, the bulk of the NO to NO_2 oxidation occurs following emission of the combustion gases, as they are dispersed in the atmosphere. Therefore, in the discussion to follow, considerations pertaining to the N_2-O_2-NO reaction system will be emphasized.

Clearly, the factors affecting NO_x emissions from fossil fuel combustion processes are more complex than the understanding of the nitrogen-oxygen fixation process as a function of chemical thermodynamic and kinetic considerations. Thus, it has become evident that chemically bound nitrogen in the fuel (coal or oil) is oxidized more readily to NO_x than highly stable molecular nitrogen, and consequently, the bound nitrogen plays a role in NO_x formation. As discussed in Section 4.2, factors such as the fuel type, the level of excess air, heat release and removal rates, mass transport (mixing of fuel and air and combustion products) also have a major bearing on the amount of NO_x produced in combustion processes. Based on the combination of kinetic and thermodynamic data with the above factors, a "first-generation" mathematical model has been developed in the present study, for predicting the effects of combustion parameters on the net generation of NO in natural gas (methane) combustion. The features, limitations, scope, and potential future extensions of this model, as well as the results observed with it to date, are discussed in Section 4.3.

Modification of either operating conditions or design features (or both) can result in lowering NO_x emissions, in accord with theoretical considerations of this complex process. Combustion modification techniques aimed at lower NO_x emissions are discussed in Section 4.4 of this report.

4.1 THEORETICAL CONSIDERATIONS OF THE N_2-O_2-NO_x REACTION SYSTEM

The atmospheric fixation of nitrogen with oxygen is represented by the following overall reaction:

$$N_2 + O_2 \rightleftharpoons 2NO \qquad (4\text{-}1)$$

The thermodynamic equilibrium constant for this reaction is given by:

$$K_{eq} = \frac{(NO)^2}{(N_2)\ (O_2)} = 21.9e^{-43,400/RT} \qquad (4\text{-}2)$$

where K_{eq} = equilibrium constant

R = 1.988 cal/g. mole/°K

T = absolute temperature, °K

(NO), (N_2), and (O_2) are the concentrations or mole fractions of the respective species, in consistent units

The value of K_{eq} (equation 4-2) is based on data from the JANAF Thermochemical Tables. As shown in Figure 4-1, for methane-air combustion at atmospheric pressure, NO formation is favored only at higher temperatures. However, NO remains a "pseudo-stable" specie even at low temperatures because of kinetic limitations of its rate of decomposition.

Figure 4-1

EQUILIBRIUM NO CONCENTRATIONS
FOR COMBUSTION OF METHANE

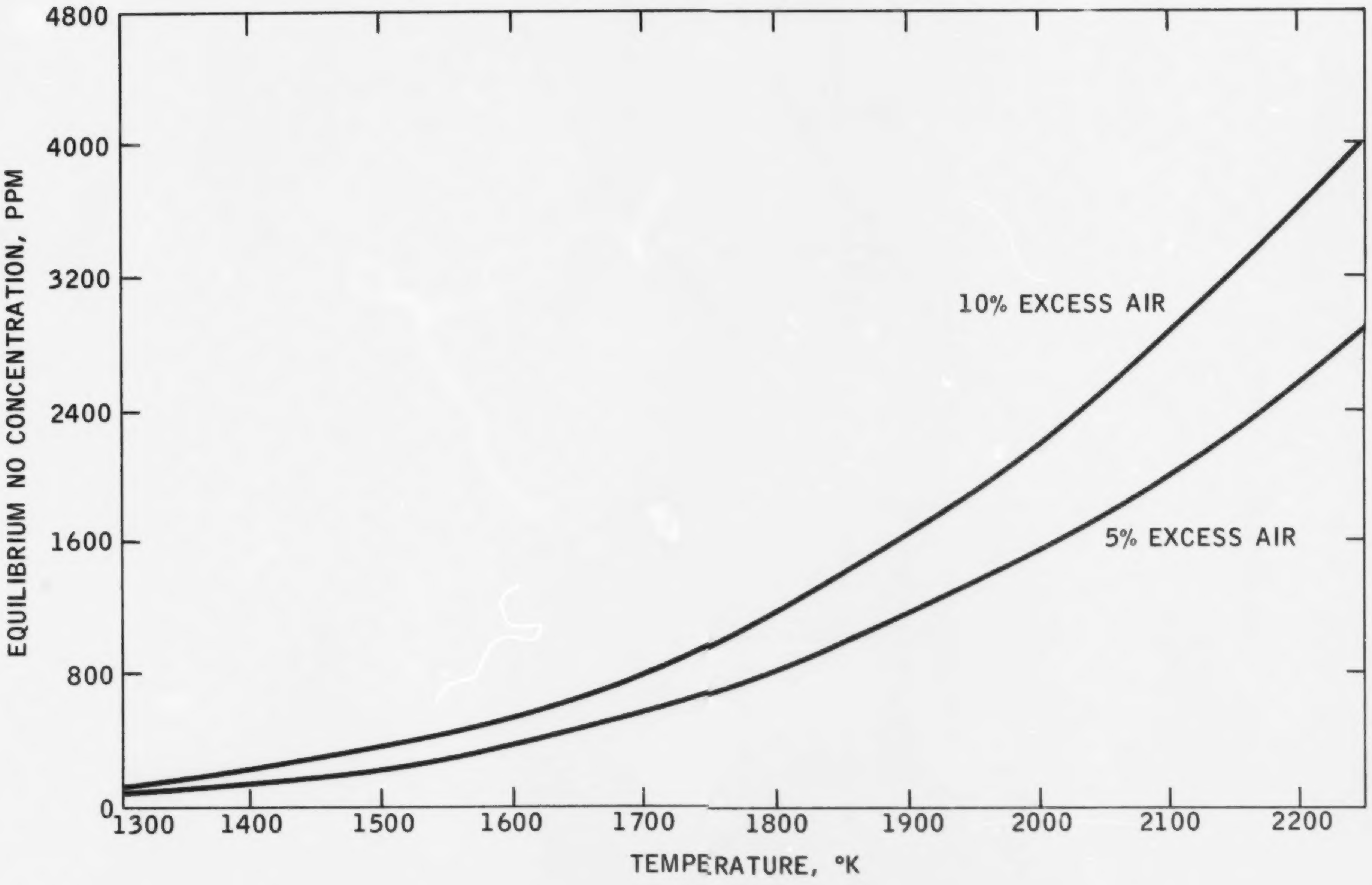
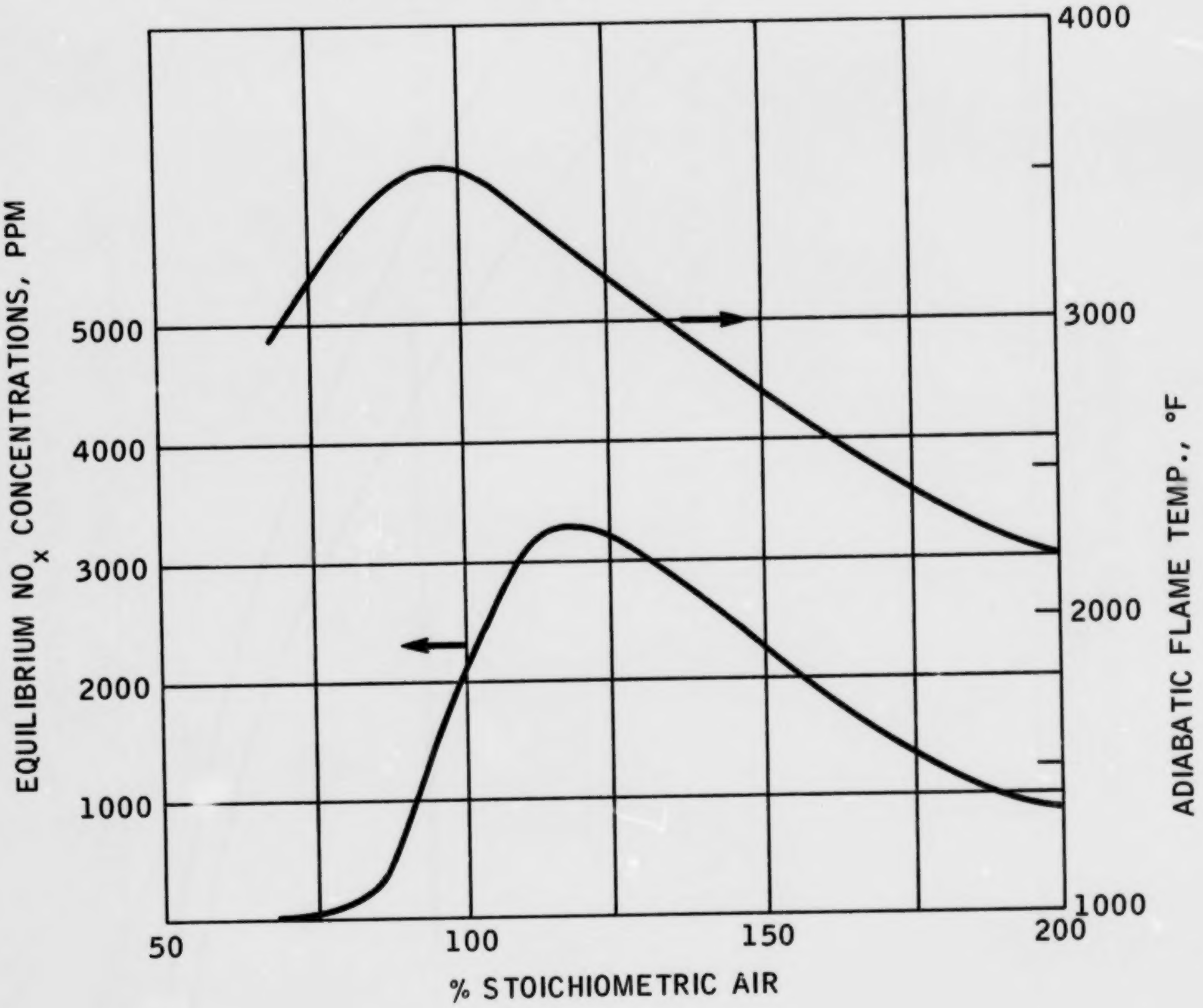


Figure 4-2

NO_x EQUILIBRIUM IN METHANE-AIR FLAMES



As shown in Figure 4-2, the equilibrium concentrations of NO is highest at about 10-15% excess air, and declines rapidly from values exceeding 3000 ppm to about 2000 at 100% stoichiometric air (i.e., zero percent excess air). This happens even though the peak adiabatic flame temperature is reached at about 95% of stoichiometric air, indicating that the availability of oxygen limits the equilibrium concentrations of NO.

As discussed before, the equilibrium concentrations of NO_2 at flame temperatures are negligibly small. The equilibrium amounts of NO and NO_2 as a function of temperature are shown in Figure 4-3.

Although NO_2 is favored by equilibrium and by kinetics over NO at lower temperatures (the rate of oxidation of NO to NO_2 has a negative temperature coefficient), the attainment of this equilibrium is relatively slow, so that usually 90-95% of the NO_x emitted in combustion processes is in the form of NO.

Experimental evidence available in the literature indicates that the mechanism of NO formation in fuel-air combustion processes is that of a chain reaction (also termed an "atomic-shuttle reaction") involving nitrogen and oxygen atoms, instead of the four-center process of Eq. 4-1. This chain reaction, first postulated by Zeldovich (4-1) as a thermal mechanism to account for his findings on NO formation in hydrogen-oxygen-nitrogen reactions, has also been confirmed by shock tube studies of N_2-O_2 mixtures, in the absence of any fuel (4-2, 4-3).

This chain reaction mechanism can be represented as follows:

$$O_2 + M \rightleftharpoons 2O + M \qquad (4\text{-}3)$$

$$O + N_2 \rightleftharpoons NO + N \qquad (4\text{-}4)$$

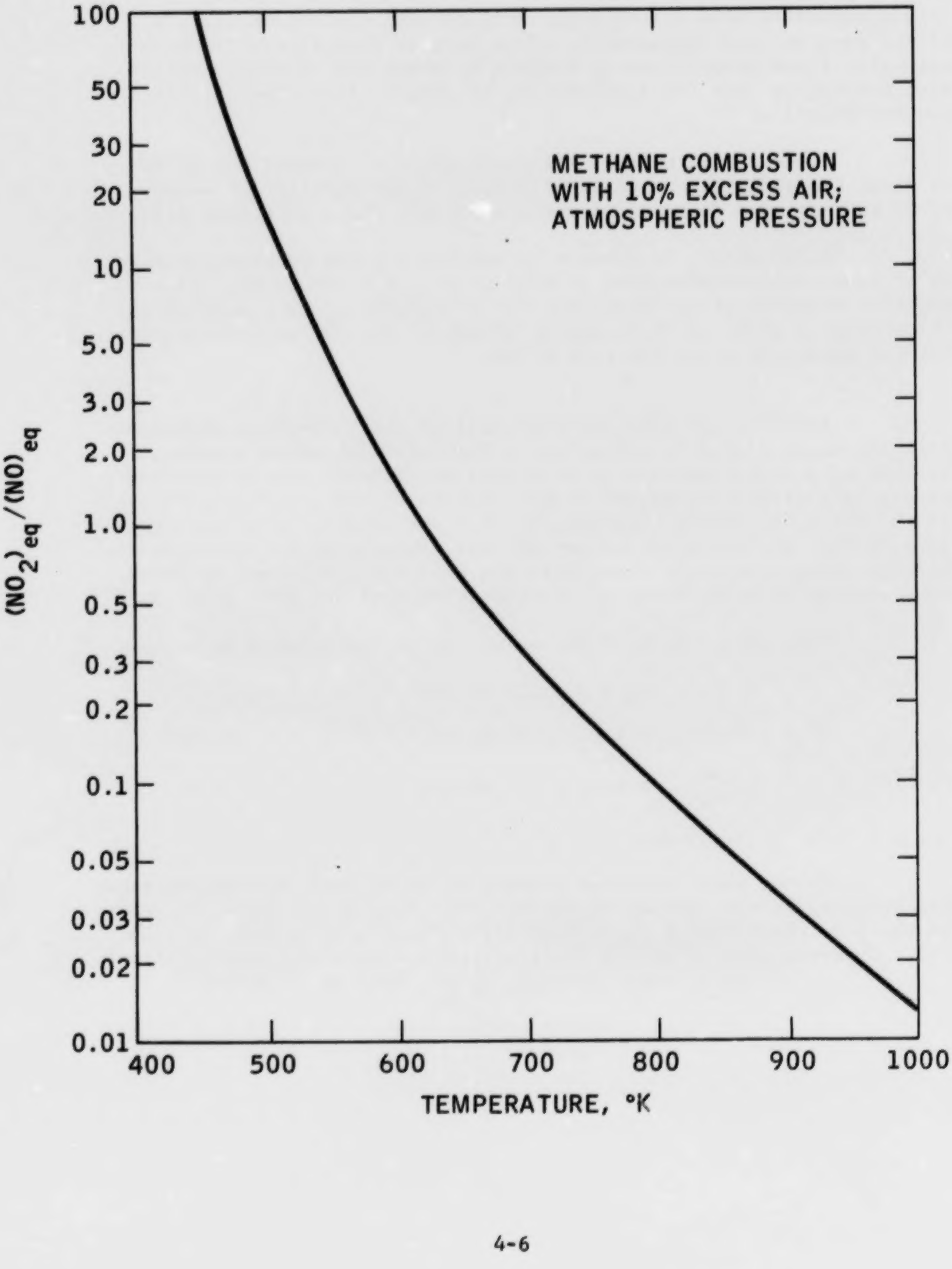
$$N + O_2 \rightleftharpoons NO + O \qquad (4\text{-}5)$$

where M is a "third" body.

In the above reaction scheme, it is assumed that oxygen atoms are supplied by the thermal dissociation of molecular oxygen, as shown in Eq. 4-3. Equilibrium is customarily assumed to hold for reaction 4-3. However, this is only a first approximation for fuel-air flames,

Figure 4-3

EQUILIBRIUM CONCENTRATIONS OF NO AND NO_2 IN COMBUSTION GASES



as experimental evidence shows that in such systems the oxygen atom concentration exceeds that calculated based on the equilibrium dissociation of molecular oxygen (4-4). This factor becomes particularly important for fuel-rich combustion processes (for which the present knowledge of kinetics is ill-defined), so that the NO formation rates calculated on the basis of the equilibrium assumption for oxygen atoms provide only lower limit values.

The rate of NO formation is very highly temperature dependent. Zeldovich (4-1) measured an activation energy of about 129 Kcal/mole for this process. The shock tube data of Glick, et al. (4-2) and of Camac and Feinberg (4-3) yield a value of about 134-135 Kcal/mole, which is in reasonable agreement with the activation energy determined by Zeldovich.

It is this very high activation energy for NO formation which is responsible for the extreme dependence of the reaction rate on temperature. The homogeneous decomposition of NO back into N_2 and O_2 has a substantially lower, but still appreciable activation energy. The NO decomposition reaction has been studied by a number of investigators, and a variety of estimates have been made for the kinetic parameters of this process (4-2, 4-3, 4-5, 4-6, 4-7, 4-8). Below 1100°K, the NO decomposition reaction is heterogeneous, between 1100°K and 1400°K both heterogeneous and homogeneous mechanisms are operative, while above 1400°K the reaction appears to be strictly homogeneous, based on these laboratory kinetic studies. The wide range of activation energies ranging from about 63 Kcal/mole (4-9) to 98 Kcal/mole (4-10) estimated by different investigators indicates that the values reported may have been affected by the particular experimental conditions under which they had been obtained.

Based on the reasonably well established values of the kinetic parameters for NO formation, the best choice for a rate expression including both NO formation and decomposition appears to be one which is consistent with both the Zeldovich chain mechanism and thermodynamic equilibrium.

Assuming steady state conditions for the "atomic shuttle reactions" 4-4 and 4-5 and the oxygen atoms to be in equilibrium with O_2 according to Eq. 4-3, the kinetics corresponding to these three equations yield the net rate of NO formation:

$$\frac{d(NO)}{dt} = A_f e^{-E_f/RT} (N_2)(O_2)^{1/2} - A_r e^{-E_r/RT} (NO)^2 (O_2)^{-1/2} \qquad (4\text{-}6)$$

g. moles/cc/sec

where A_f, A_r and E_f, E_r are the pre-exponetial factors and activation energies of the forward and reverse rate expressions, respectively. The concentration terms (N_2), (O_2), and (NO) are in units of g. moles/cc, and R and T are the gas constant and the absolute temperature, in units of cal/g. mole/°K and °K, respectively.

It should be noted that the steady state treatment of Eq. (4-3)-(4-5) assumes that $(O_2) \gg (NO)$, resulting in the relatively simple expression of Eq. (4-6). Also, the Zeldovich chain mechanism shows an inverse dependence of the NO decomposition rate on the square root of the oxygen concentration, which is in agreement with shock tube studies of the N_2-O_2 reaction (4-2, 4-3). Clearly, the Zeldovich mechanism is not more than a convenient simplification of this very complex reaction system. For example, Camac and Feinberg (4-3) have shown that an important elementary reaction step in the decomposition of NO is

$$2NO \rightarrow N_2O + O \qquad (4\text{-}7)$$

which results in the generation of more oxygen atoms. For the sake of simplicity and overall consistency, such additional reaction steps have not been included in the present kinetic treatment, and in the development of our mathematical model which is discussed in Section 4.3.

For the rate of formation of NO, we selected the rate expression based on the data of Glick, et al. (4-2) as the most representative:

$$\frac{d(NO)}{dt} = 9 \times 10^{14} e^{-135,000/RT} (N_2)(O_2)^{1/2} \qquad (4\text{-}8)$$

g. moles/cc/sec

Eq. (4-8) is in numerical agreement with the rate expression based on the data of Camac and Feinberg (4-3):

$$\frac{d(NO)}{dt} = 7 \times 10^{14} e^{-134,300/RT} (N_2)(O_2)^{1/2} \qquad (4\text{-}9)$$

g. moles/cc/sec

over the temperature range of interest for fossil fuel combustion processes.

Combining Eqs. 4-8 and 4-2, the net rate of NO formation is given by:

$$\frac{d(NO)}{dt} = 9 \times 10^{14} e^{-135,000/RT} (N_2)(O_2)^{1/2} - 4.1 \times 10^{13} e^{-91,600/RT} (NO)^2 (O_2)^{-1/2} \qquad (4\text{-}10)$$

g. moles/cc/sec

All terms in the above rate expression are in the units specified for Eq. (4-6). The net rate of NO formation of Eq. (4-10) provides the basis of our mathematical model of NO formation in methane combustion processes, discussed in Section 4.3.

The consequence of the thermodynamics and kinetics of NO formation and decomposition reactions is that NO_x emission control by combustion modification must consist of lowering the effective flame temperature. Also, the exposure of combustion gases to the highest temperatures prevailing in the combustion equipment must be minimized. Furthermore, the availability of the reactants, oxygen and nitrogen must be limited.

As will be discussed later, it is not practical, based on both technical and economic considerations to limit the supply of available nitrogen, as the high flame temperatures prevailing under enriched oxygen firing more than compensate for any effect of reduced nitrogen concentrations on NO_x emissions. Thus, in practice, the supply of excess air must be kept as low as possible to reduce the level of NO_x emissions. These considerations, as well as other factors influencing NO_x formation in fossil fuel combustion processes are discussed in the following section of this report.

4.2 FACTORS INFLUENCING NO_x FORMATION IN FOSSIL FUEL COMBUSTION PROCESSES

As outlined in Section 4.1, the formation of NO_x in fossil fuel combustion processes is profoundly affected by thermodynamic and kinetic rate factors. In addition, other factors such as fuel type and composition, heat and mass transport rates in the combustion equipment, and finally operating and design variables contribute significantly to NO_x emissions.

Some of the factors influencing NO_x formation are a direct consequence of the theoretical considerations discussed above. These factors and specifically the trends which may be utilized for lowering NO_x emissions are discussed in this section. Also, what is known about the effects of fuel type and composition will be discussed. Specific operating and design changes, generally based on the application of theory will be discussed in detail in Section 4.4.

4.2.1 Effect of Temperature-Time Profile (Heat Release and Removal Rates) and Reactant Concentrations

A direct consequence of the thermodynamics of the

$$N_2 + O_2 \rightleftharpoons 2NO$$

reaction system is that NO can be formed only at high temperatures, as dictated by Eq. 4-2. In stationary fossil fuel combustion equipment, the residence time available for NO formation is in general insufficient to reach the equilibrium NO concentrations corresponding to the peak flame temperatures. Therefore, the temperature-time history of the combustion process, i.e., kinetics, has a very important bearing on the ultimate concentration of NO produced.

Both the rates of NO formation and decomposition are highly temperature dependent. Since NO formation takes place at concentration levels below equilibrium, the kinetics of formation are usually more important then the kinetics of decomposition. However, as heat is removed from the hot combustion gases, the NO formation rate ceases to be important, and depending on the rate of heat removal, some decomposition may take place. The extent of NO decomposition is usually quite modest in magnitude, because this reaction is quite slow (due to its high activation energy), and its rate becomes vanishingly small below 2300-2400°F, under typical combustion conditions. Thus, the NO concentration becomes "frozen", and since NO oxidation to NO_2 is unimportant (as discussed in Section 4.1), the "frozen" concentration of NO represents the level of NO_x emitted. These arguments will be illustrated quantitatively in Section 4.3, based on calculations made using Esso's mathematical model of NO formation, which was developed during the course of this study.

The outstanding conclusions based on the known chemistry of NO formation and decomposition are as follows:

(a) The temperature-time profile of the combustion gases should be controlled in such a manner that the residence time at the peak temperatures is kept to a minimum. The manner in which this concept may be achieved varies, of course, with the type of fossil fuel combustion equipment. For example, on the laboratory scale, combusting methane or propane gas fuel with air in a flat flame burner, the desirability of rapid heat dissipation has been demonstrated by Grumer, et al. (4-11) (4-12). Flame temperatures were reduced by flue gas recirculation into the combustion zone, resulting in lower NO_x emissions. Using a porous ceramic burner capable of higher rates of radiant heat dissipation, similar reduction in NO_x emissions were obtained (4-13).

On the other extreme of combustion equipment scale, power plant boiler furnaces can be designed in such a way that the heat generated by combustion is more rapidly dissipated. As will be discussed in Section 4.4, combustion modifications such as two-stage combustion (where heat is removed from oil or gas flames before the addition of secondary air required for complete burn-out of fuel and carbon monoxide), or tangential firing where heat is transferred to the "water-walls" of the furnace at increased rates, result in substantial reductions of NO_x. The above factors indicate that for minimizing NO_x formation, high heat transfer, or "quench rates" are desirable.

If possible, high heat release rates resulting in high peak temperatures should be avoided. This requirement is, to some extent, contrary to the design of furnaces having high thermal efficiency. While the volumetric heat release rate increases with the cube of the linear furnace dimension, the amount of available surface increases only with the square of the linear dimension. Thus, as the trend in steam-electric power generation is toward larger and larger boiler/turbine installations, higher firing rates are required. This is achieved by the installation of multiple burners, resulting in flames which fill a larger portion of the furnace. However, the relative amount of cooling surface is decreased, and the net result is higher flame temperatures, and higher NO_x emissions, unless control measures are applied.

(b) The availability of reactants, nitrogen and oxygen, must be limited to the degree consistent with efficient operation. As will be discussed later, limiting the amount of nitrogen (enriched air firing) is unattractive both technically and economically. Firing with "pure" oxygen (containing only small amounts of nitrogen) results in extremely high flame temperatures, which more then counterbalance any advantage derived from limiting the amount of nitrogen. This point will be illustrated in Section 4.3 by calculations which show high NO_x emissions even when 99.9% pure oxygen is used for burning natural gas. (Furthermore, in the case of coal or oil fuel, the chemically combined nitrogen provides a "built-in" supply of reactive nitrogen for NO_x formation).

Thus, only the reduction of the level of excess air (i.e., available oxygen for NO_x formation) is a practical approach to limiting reactant concentration. At low excess air levels the flame temperature increases, (as discussed in Section 4.1), but this factor is outweighed by limiting the available oxygen for NO_x formation. Therefore, low excess air firing is a powerful technique for NO_x reduction, particularly in combination with other combustion modification techniques. The evidence for the success of low excess air firing will be discussed in subsequent sections of this report.

(c) Mass transport, or mixing of fuel, air and combustion products also affects NO_x formation. The theoretical treatment of NO chemistry does not take into account localized inhomogeneities in fuel/air distribution, but deals with the problem on the basis of a completely mixed system. This, of course, is not the case in the combustion of oil spray droplets or coal particles.

While the overall fuel/air ratio is the same, it is easy to visualize a variety of situations where fuel, or air are in excess in localized portions of the combustion zone. Thus, if the bulk of the combustion process can be made to occur under relatively fuel-rich conditions, the NO concentration will be low because of the local "low excess air" (or even substoichiometric) conditions. While this type of combustion takes place, heat is removed via radiation and convection from the combustion gases. Then, the air supply must be adjusted so as to ensure the complete burn-out of the fuel and carbon monoxide produced under fuel-rich conditions. However, this process will occur at lower temperatures, resulting in reduced net levels of NO_x emissions.

The above concepts are theoretically sound, but their reduction to practice depends greatly on the particular applications. For example, imbalances in fuel/air distribution may create formidable problems in pulverized coal combustion, where even low excess air firing has not been demonstrated to date, except for laboratory experiments which indicated that NO_x emissions could be reduced only at the cost of less than complete burn-out of the fuel (4-14). In pulverized coal firing, the small coal particles burn more rapidly than the larger ones in the particle size distribution, as the burning rate varies inversely with particle diameter. The problem of applying low excess air firing, two-stage combustion or other combustion modififcations consisting of fuel-rich environments still requires a thorough study, particularly for coal combustion.

Finally, as regards mass transport effects, the influence of internal recirculation, or backmixing of the combustion products should not be overlooked. Backmixing also results in lowering peak flame temperatures, in addition to diluting the concentration of available oxygen, which should produce lower levels of NO_x emissions. Particularly with smaller combustion equipment, deliberate design aimed at internal recirculation should prove to be quite effective for NO_x control.

4.2.2 Effect of Fuel Type and Composition

Fuel type and composition may have an important effect on NO_x emissions from combustion processes. Based on the "standard" average emission factors, summarized in Table 3-2, (4-15), NO_x emissions are highest from coal firing, followed by oil firing, while gas firing should result in the lowest levels of NO_x emissions.

The above "ranking" of fuel types can be rationalized simply on the basis of adiabatic flame temperatures reached under identical combustion conditions. Coal flames have the highest theoretical adiabatic flame temperatures, oil flames are intermediate, while gas flames produce the lowest adiabatic temperatures.

The actual situation is, of course, much more complex than the above correlation of higher NO_x emissions with increasing adiabatic flame temperatures. The chemically bound nitrogen in the fuel also plays a role in NO_x formation, i.e., the higher the fuel nitrogen content, the more NO_x is expected to be formed. This factor also correlates with the NO_x-forming tendencies of coal, oil and gas, which contain chemically bound nitrogen in the above order (natural gas contains virtually no bound nitrogen).

While quantitative data are not available at present on the rate of conversion of fuel nitrogen to NO_x, it is theoretically predictable that oxygen should attack the weaker carbon-nitrogen bonds of fuel molecules more readily than the very strong $N \equiv N$ bond in molecular nitrogen.

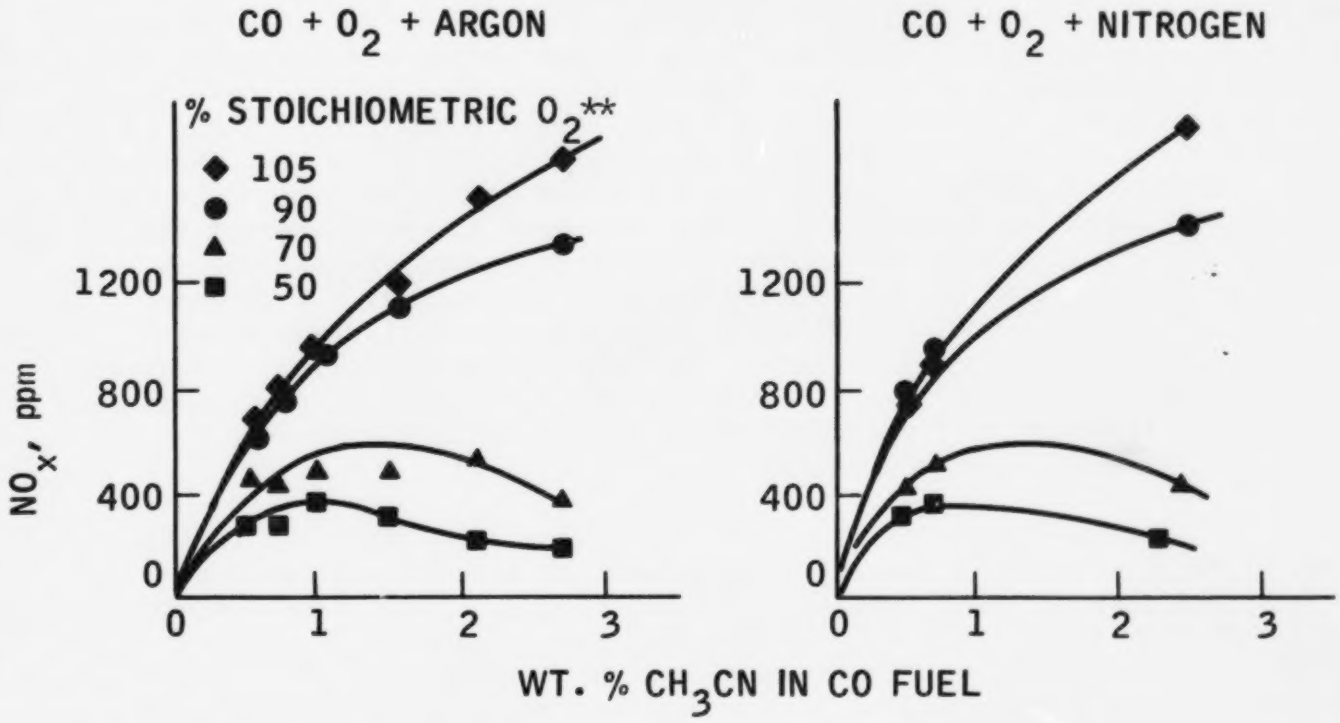
The fact that fuel nitrogen plays a role in NO_x formation has been established beyond any doubt. The following discussion summarizes the available experimental evidence.

In flat flame laboratory experiments, J. T. Shaw and A. C. Thomas of BCURA (4-16) have shown that the addition of organic nitrogen compounds (methyl cyanide, sec-butylamine, or pyridine) to carbon monoxide fuel enhances NO_x formation, with or without molecular nitrogen present in the CO-oxidizer mixture. As much as 1200 ppm NO_x was measured both in the presence, and in the absence of molecular nitrogen, in the low temperature combustion of CO (860-1145°K). Apart from NO_x formation in the absence of molecular N_2, the low temperatures obtained in these experiments exclude substantial NO_x formation from the atmospheric N_2-O_2 reaction, and therefore, the important role of nitrogen in the fuel was clearly established for low temperature combustion processes. Typical data obtained by Thomas and Shaw are illustrated in Figure 4-4, for CO/O_2/argon and $CO/O_2/N_2$ mixtures, with methyl cyanide as the nitrogen containing additive. The maximum levels of NO_x found correspond to about 40-50% conversion of the fuel nitrogen to NO_x. The actual NO_x levels shown in Figure 4-4 have been reported by the above authors to be incorrect, because the nitrogen component additives were not taken into account in computing combustion stoichiometry (4-16A). Nevertheless, the contribution of fuel nitrogen oxidation to NO_x formation is still demonstrated by this work.

Perhaps an even more dramatic demonstration of the role of bound fuel nitrogen in NO_x formation has been observed in fluidized bed coal combustion experiments. As will be discussed later, fluidized bed combustion takes place at average bed temperatures of only 1600-1700°F, so that

Figure 4-4

EFFECT OF ADDED NITROGEN COMPOUND ON NO_x FORMATION IN CO COMBUSTION*



* After reference (4-16)

** Based on CO only. Actual % stoichiometric O_2 decreases from nominal levels indicated as the wt. % CH_3CN in the fuel increases.

virtually no NO_x formation should result from the direct N_2/O_2 reaction. However, all the measurements reported by NAPCA contractors (Pope, Evans and Robbins, and Argonne National Laboratory) indicated that the NO_x emission levels were about the same as from comparably sized conventional combustion equipment.

In one set of fluidized bed combustion experiments, Argonne National Laboratory (4-17) substituted argon for the nitrogen of the air. The NO_x levels in the flue gases were essentially the same, over 500 ppm with or without N_2 present. Again, the evidence is unequivocal for the participation of bound fuel nitrogen in NO_x formation in low temperature combustion processes.

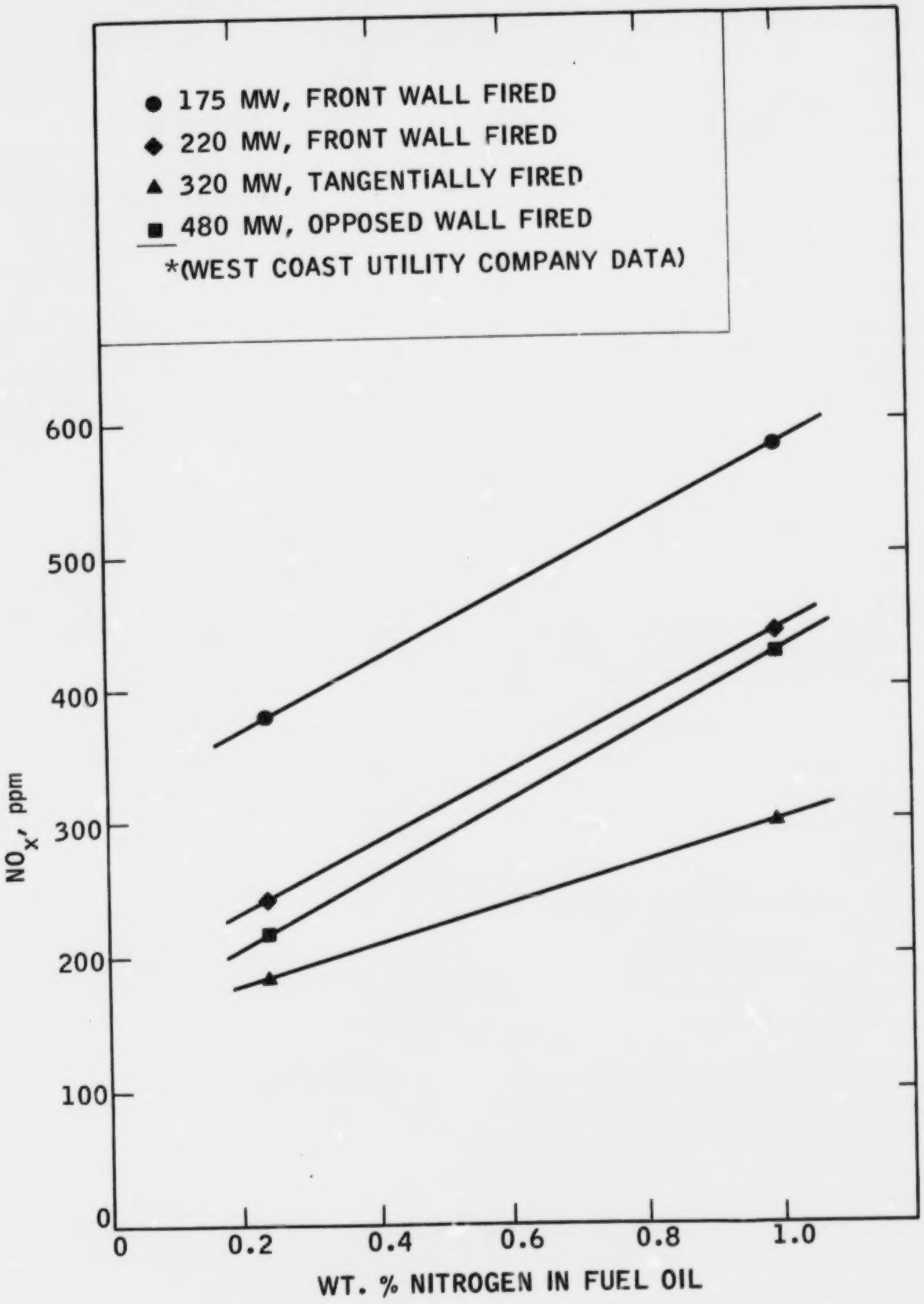
At higher temperatures, it is expected that the contribution of bound fuel nitrogen to NO_x formation should become less important. Clearly, at or near equilibrium combustion conditions the source of the nitrogen is immaterial, i.e., whether it is contained in the fuel or the air, the NO_x levels will be the same. However, in the region intermediate between low temperatures and equilibrium flame temperatures, actual fossil fuel combustion processes take place under non-equilibrium conditions. Thus, as the peak flame temperatures increase, one would expect decreasing, but still substantial contributions of the fuel nitrogen to overall NO_x emissions with increasing temperatures. Data obtained in the course of the present study from a West Coast electric utility company (4-18), which used two types of fuels: (1) cracked residual fuel oil with a nitrogen content of 1.0 wt %, and a paraffinic, low nitrogen, sulfur and metals containing fuel oil (nitrogen content 0.24 wt %), qualitatively demonstrate the increase in NO_x with fuel nitrogen content. The NO_x emissions measured at the two different fuel nitrogen levels are shown in Figure 4-5, for a variety of furnace types and sizes.

Another directional indication of the role of nitrogen in the fuel in NO_x formation is the correlation made by Elshout and van Duren (4-19), based on the data compiled of Smith (4-20). These data concern emissions from power plant boilers, in the range of about 270-400 ppm (corrected to 12% CO_2 in the flue gas). With the fuel nitrogen content varying between 0.4 and 1.2 wt %, the flue gas NO_x content appears to be linearly increasing with fuel nitrogen.

Finally, recent data obtained in distillate fuel oil combustion using organic nitrogen compounds as additives (4-21), also correlate NO_x emissions with fuel nitrogen content. Thus, the role of nitrogen in the fuel in NO_x formation is definitely established under a variety of combustion conditions, and with different fuel types. However, as discussed before, kinetic rate data obtained with representative fuel nitrogen compound types are required for a quantitative interpretation of the fuel nitrogen effect.

Figure 4-5

EFFECT OF FUEL NITROGEN ON NO_x EMISSIONS*



Returning to the effect of fuel type, rather than that of fuel composition, even the atmospheric N_2-O_2 reaction is complicated by the coupled effects of heat release and heat removal rates. While coal, oil and gas are theoretically capable of developing flame temperatures in the above order, under adiabatic conditions the rates of heat transfer from such flames also vary with the fuel type. Coal and oil are more prone to burn under luminous flame conditions, which enhances radiative heat transfer. In general, the emissivity of "blue" gas flames is low, and therefore, radiative heat transfer rates are also lower. The net result is that gas flames are "quenched" more slowly by radiative heat transfer, resulting in sometimes dramatic deviations from the "standard" emission rates for these fuel types.

In smaller scale combustion equipment, where heat transfer rates by convection and radiation are about the same order of magnitude, the above considerations are only of secondary importance. However, in large combustion installations, particularly in large power plant boiler furnaces where virtually all the heat transfer is radiative, such "quenching rate" effects can become very important.

In fact, a reversal in the order of magnitude of NO_x emissions from oil and gas flames has been reported in two large 750 MW boilers at the Moss Landing Station of the Pacific Gas and Electric Company (4-22). Firing with natural gas, without combustion modification controls, NO_x emissions of about 1500 ppm were measured (these emissions were subsequently reduced to low levels by a successful combination of low excess air firing with two-stage combustion, as will be discussed later). Under similar conditions, oil firing, without controls, resulted in only about 400 ppm NO_x emitted in the flue gas.

As discussed earlier in this section, in large furnaces the available heat transfer area becomes limiting at the high heat release rates required. Therefore, it is conceivable that low emissivity gas flames under such conditions are quenched more slowly than oil flames (or coal flames), resulting in high NO_x emissions, unless control methods are applied.

4.2.3 Summary of Major Factors

The brief summary below is intended to highlight the major factors known to influence NO_x emissions from combustion processes.

(A) Excess Air

Low excess air firing results in reducing NO_x emissions. The lowest level of excess air permissible without operating problems depends on the combustion process and the type of fuel used.

(B) Heat Release and Removal Rates

High heat release rates lead to increased NO_x emissions, because of the extreme sensitivity of NO_x formation equilibrium and kinetics to peak temperatures. High heat removal (or quenching rates) are desirable, on the other hand, for stationary combustion processes, as they limit the exposure of the combustion gases to the highest temperatures. Thus, kinetic limitations are imposed on the amount of NO_x formed in the process.

(C) Mass Transport and Mixing

The distribution of fuel and air, and then mixing with combustion gases can affect NO_x emissions. Deliberate "imbalances" created to consume most of the fuel under fuel rich conditions may result in reducing NO_x emissions. Similarly, internal recirculation, or backmixing of combustion gases dilutes the primary flame zone, reducing its temperature, which is desirable for limiting NO_x formation rates.

(D) Fuel Type and Composition

Fuel type affects NO_x formation both through the theoretical flame temperatures attainable (coal $\gtrsim$ oil > gas), and through the rate of radiative heat transfer (coal > oil > gas). These coupled factors may balance each other, but in general for small to intermediate combustion installations it is a good "rule-of-thumb" to rank NO_x emission forming tendencies in the order: coal > oil > gas. For large installations, limited evidence indicates that this order may be reversed, presumably due to the shift in heat release/heat removal ratios.

As regards fuel composition, the role of chemically bound nitrogen in NO_x formation is definitely established. The extent of contribution of nitrogen in the fuel varies with the temperature level of the combustion process, from being all-important at low temperatures (e.g., fluidized bed combustion), to negligible amounts near equilibrium. Further studies are needed to provide a quantitative perspective on this effect.

4.3 MATHEMATICAL MODEL OF NO FORMATION AND DECOMPOSITION IN NATURAL GAS COMBUSTION

In principle, based on theoretical considerations and the factors affecting NO_x emissions from combustion sources, it is possible to provide a quantitative description of the net rate of NO formation. The formulation of a mathematical model which takes into account chemical thermodynamics and kinetics, the effects of heat and mass transport, and the operating and design parameters is an exceedingly complex process. For this reason, it was decided to formulate an idealized "first-generation" model, capable of predicting directional effects on NO formation and decomposition. This model was formulated after a thorough review of the pertinent literature, with the objective of providing maximum flexibility for future additions and modifications to the model.

The ultimate goal of developing such a mathematical model is to use it for predicting NO formation rates under realistic conditions, to compare the model predictions with actual laboratory and test data, and eventually to use it for guiding the design of combustion equipment having reduced NO_x emissions. In this section, the features, scope, and range of applicability of Esso's NO formation model are outlined. In addition, requirements are indicated for future modifications to this model to broaden its scope, including the additions needed for predicting the fate of unburned fuel and carbon monoxide.

Modeling or kinetic calculations of NO_x formation and decomposition reported in the literature have dealt largely with emissions from internal combustion engines, or with attempts to fixate atmospheric nitrogen by freezing out NO. In automotive emission oriented studies carried out by Starkman and co-workers (4-23), (4-24), (4-25), (4-26), and by Newhall (4-27), (4-28), by Eyzat and Guibert (4-29, 4-30, 4-31), and others, the quenching rate is usually so high (except for gas turbine engines) that the NO_x emissions correspond nearly to the peak NO concentrations reached near equilibrium. Studies aimed at atmospheric fixation of nitrogen (4-32, 4-33) are of little consequence from the standpoint of NO_x emission control, as the residence time available in stationary combustion equipment is usually too short for NO decomposition to be a major factor.

4.3.1 DESCRIPTION OF THE ESSO MATHEMATICAL MODEL

The Esso model of net NO formation in natural gas combustion is idealized by using premixed, gaseous hydrocarbon fuel/air feed. To simulate natural gas combustion, methane was selected as the fuel. The relevant features of this model are as follows:

(a) One-dimensional, homogeneous gas phase reaction system.

(b) Specified flow velocity, pressure, and flow area profiles.

(c) Heat transfer specified optionally by

(i) heat transfer rates profiles
(ii) heat transfer coefficients and wall temperature profiles
(iii) gas temperature profiles
(iv) quenching rate profiles

(d) Heat generation described by two-step overall kinetics of hydrocarbon oxidation to CO, followed by CO combustion to CO_2.

(e) Zeldovich-type kinetics used to calculate NO concentrations.

(f) Multiple point injection of fuel, air or flue gases, which makes it possible to simulate two-stage combustion or flue gas recirculation.

In detail, the mathematical model consists of these basic parts:

- Detailed kinetics of the fuel combustion and NO formation and decomposition processes.
- Detailed description of the flow of material within the flame.
- Detailed description of the heat flow within the flame and to the surroundings.

The modeling considerations for each of these items will be discussed in turn. Heat and material balances will then be developed and the solution procedure will be briefly described.

4.3.1.1 Kinetic Model

Combustion of a hydrocarbon fuel (F) in the gaseous state is considered to occur in two stages:

$$a(F) + b(O_2) \xrightarrow{k_{11}} c(CO) + d(H_2O) \qquad (4\text{-}11)$$

$$2(CO) + (O_2) \xrightarrow{k_{12}} 2(CO_2) \qquad (4\text{-}12)$$

where a, b, c, d are stoichiometric coefficients; and k_{11}, k_{12} are specific reaction rate constants.

The rate constants, in turn, are assumed to be of the Arrhenius form:

$$k = A \exp(-E/RT)$$

where A is the frequency factor;
E is the activation energy;
R is the universal gas constant; and
T is the absolute temperature.

From the literature for hydrocarbon fuel combustion, the rate of reaction ($\mathcal{R}$) for **(4-11) and (4-12) have been found to be of the form:**

$$\mathcal{R}_1 = k_1(\rho X_F)^{\alpha_1}(\rho X_{O_2})^{\beta_1}(\rho X_{H_2O})^{\gamma_1} \qquad (4\text{-}13)$$

and

$$\mathcal{R}_2 = k_2(\rho X_{CO})^{\alpha_2}(\rho X_{O_2})^{\beta_2}(\rho X_{H_2O})^{\gamma_2} \qquad (4\text{-}14)$$

where X represents mole fractions;
ρ is the molar density of the gas; and
α, β, γ are empirical constants.

The above rate equations have been fitted by kinetic parameters measured for methane combustion. The detailed chemistry of this process is complex, as is typical for gas phase free radical chain reactions. Under steady state conditions, the rate controlling steps appear to be the reactions of methane and carbon monoxide (an intermediate product) with hydroxyl free radicals (4-34).

$$CH_4 + OH \rightleftharpoons CH_3 + H_2O \qquad (4\text{-}15)$$

$$CO + OH \rightleftharpoons CO_2 + H \qquad (4\text{-}16)$$

Corresponding to these rate controlling steps, the "overall" kinetics of methane combustion can be described by a two-step sequence of reactions, in the form of equations 4-11 and 4-12:

$$CH_4 + 3/2\ O_2 \rightleftharpoons CO + 2H_2O \qquad (4\text{-}17)$$

$$CO + 1/2\ O_2 \rightleftharpoons CO_2 \qquad (4\text{-}18)$$

The rates of combustion of methane and carbon monoxide have been determined by Morgan in a jet mixed reactor, under fuel-lean conditions (4-35).

$$\frac{-d(CH_4)}{dt} = 4.7 \times 10^{15} e^{-56,000/RT} (X_{CH_4})(X_{O_2})^{1/2}(X_{H_2O})^{1/2}\left(\frac{P}{RT}\right)^2 \tag{4-19}$$

$$-\frac{d(CO)}{dt} = 1.8 \times 10^{10} e^{-25,000/RT} (X_{CO})(X_{O_2})^{1/2}(X_{H_2O})^{1/2}\left(\frac{P}{RT}\right)^2 \tag{4-20}$$

where combustion rates are in units of g. moles/l./sec., P is the absolute pressure in atmospheres, and X represents the mole fraction of the reacting species, as in equations 4-13 and 4-14. These "lean" methane combustion rates are very high, and can be accomplished only under the idealized conditions of a jet-stirred combustor. In using Morgan's rate expressions in our mathematical model, it has been recognized that the equations apply only to fuel-lean conditions, and that fuel and CO burn-out rates predicted by the model would be very high.

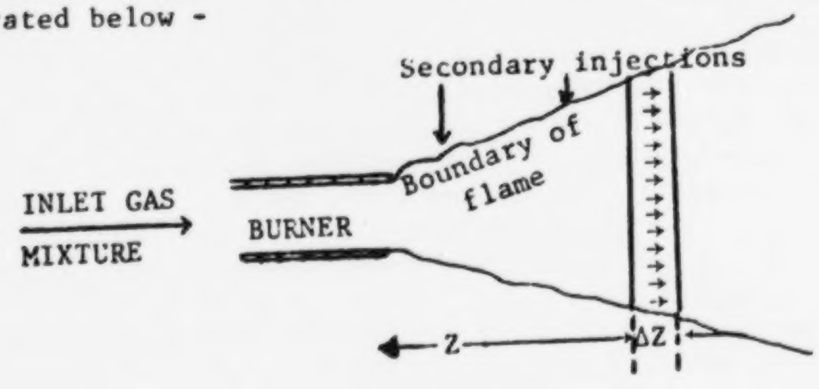
The nitric oxide reactions are treated completely separately from the combustion reactions - i.e., decoupled. The nitric oxide kinetics are assumed to follow the Zeldovich mechanism, as represented by equations 4-3, 4-4, and 4-5. The expression for the rate of production of nitric oxide is then:

$$\mathcal{R}_{NO} = k_{NO}^{(F)} (\rho X_{N_2})(\rho X_{O_2})^{\frac{1}{2}} - k_{NO}^{(R)} (\rho X_{NO})^2/(\rho X_{O_2})^{\frac{1}{2}} \tag{4-21}$$

where $k_{NO}^{(F)}$ and $k_{NO}^{(R)}$ are rate constants for the production and removal, respectively, of nitric oxide, and are of the Arrhenius form, as given by equation 4-10.

4.3.1.2 Mass Flow Model

The flame is considered to emanate from a single, stationary burner. A mixture of fuel and air (or any gas containing oxygen) is fed into the burner. The burning gases move in one-dimensional plug flow, and the pressure within the flame is uniform and constant. Thus, diffusion of momentum and mass are neglected. Gases of arbitrary composition may be injected at one or more points along the flame. Finally, the perimeter of the boundary of the flame and the cross-sectional area for mass flow within the flame must be specified, but may vary along the length of the flame. The flame, including a differential cross section located at a distance Z from the burner, is illustrated below -



4.3.1.3 Heat Flow Model

Within the flame, heat is assumed to move only by convection in one-dimensional plug flow. (Radiation and conduction of heat are neglected.) However, heat transfer from the flame to the surroundings is assumed to occur by radiation and convection, with conduction neglected.

4.3.1.4 Material Balances

Material balances for the total molar flow rate of gas, G(moles/sec), and the mole fractions of all chemical species (Fuel, O_2, CO, H_2O, CO_2, N_2, NO) can be written for the differential section of flame in the previous illustration. The resulting differential material balance equations are as follows.

Total gas rate -

$$\frac{1}{\mathbf{a}}\frac{dG}{dZ} = (c+d-a-b)\,r_1 - r_2 \qquad (4\text{-}22)$$

where $\mathbf{a}$ is the cross-sectional area of the flame at distance Z. This equation states that the change in the molar gas rate across a differential section is due to the change in moles in the combustion reactions 4-11 and 4-12 within the section. (The mole changes due to the nitric oxide reactions are neglected.)

Carbon Monoxide -

$$\frac{1}{\mathbf{a}}\frac{d(GX_{CO})}{dZ} = c\,r_1 - 2\,r_2 \qquad (4\text{-}23)$$

This equation states that the change in the molar flow rate of CO across a differential section is due to the production of CO in reaction 4-11 and the loss of CO in reaction 4-12 within the section. Similar interpretations can be given to the remaining material balances.

Fuel -

$$\frac{1}{a}\frac{d(GX_F)}{dZ} = -a\mathcal{R}_1 \qquad (4\text{-}24)$$

Oxygen -

$$\frac{1}{a}\frac{d(GX_{O_2})}{dZ} = -b\mathcal{R}_1 - \mathcal{R}_2 \qquad (4\text{-}25)$$

Steam -

$$\frac{1}{a}\frac{d(GX_{H_2O})}{dZ} = d\mathcal{R}_1 \qquad (4\text{-}26)$$

Carbon Dioxide -

$$\frac{1}{a}\frac{d(GX_{CO_2})}{dZ} = 2\mathcal{R}_2 \qquad (4\text{-}27)$$

Nitrogen -

$$\frac{1}{a}\frac{d(GX_{N_2})}{dZ} = 0 \qquad (4\text{-}28)$$

Nitric Oxide -

$$\frac{1}{a}\frac{d(GX_{NO})}{dZ} = \mathcal{R}_{NO} \qquad (4\text{-}29)$$

Note that the nitrogen and oxygen consumed in the nitric oxide reactions were considered to be negligible.

The boundary conditions for these differential equations are the inlet and secondary injection feed rates and compositions.

4.3.1.4 Heat Balance

The heat balance for the differential section of flame is

$$G\bar{c}_p\frac{dT}{dZ} = \mathcal{R}_1\Delta H_1 + \mathcal{R}_2\Delta H_2 - SQ \qquad (4\text{-}30)$$

where $\bar{c}_p$ is the average heat capacity of the gas mixture, computed as a function of temperature for each chemical specie;

ΔH is the heat of reaction, computed as a function of temperature;

S is the perimeter of the flame at distance Z; and

Q is the heat flux to the surroundings.

This equation states that the change in gas temperature across a differential section is due to the heat generated by combustion reactions within the section and the heat transferred to the surroundings. Note that the heat effects of the nitric oxide reactions are considered to be negligible. The boundary conditions for this differential equation are the inlet and secondary injection feed temperatures.

The heat flux, Q, may be specified directly and may vary along the length of the flame. The heat flux is also included directly within the model for heat transfer by convection and/or radiation via the relation:

$$Q = C_c(T-T_S) + C_R(T^4-T_S{}^4) \qquad (4\text{-}31)$$

where C_c is the convection heat transfer coefficient;

C_R is the radiation heat transfer coefficient; and

T_S is the constant, uniform temperature of the surroundings.

When the heat flux cannot be readily specified by one of the above methods, the heat balance may be ignored in favor of directly specifying the gas temperature profile along the entire length of the flame. A semi-direct way of designating the gas temperature profile is also available through a specified quench rate (QR). The QR is defined as the rate of temperature change (degrees/second) of the gas as it moves down the flame. The gas temperature is then computed from:

$$\frac{1}{\mathcal{A}}\,\frac{dT}{dZ} = \frac{QR}{G/\rho} \qquad (4\text{-}32)$$

In the program a quadratic form of the QR is used:

$$\frac{dT}{dt} = A + BT_{°K} + CT_{°K}^2, \ °K/sec. \qquad (4\text{-}33)$$

4.3.1.5 Equation of State

The perfect gas law is assumed to be valid for the gases in the combustion system. The molar gas density is then computed from:

$$\rho = \frac{P}{RT} \qquad (4\text{-}34)$$

where P is the pressure.

4.3.1.6 Method of Solution

Equations 4-22 to 4-28, and 4-30 must be integrated to determine the temperature, the gas flow rate, and the mole fractions of fuel, O_2, CO, H_2O, CO_2, and N_2 along the entire length of the combustor. This integration is done by means of an implicit scheme in which the differentials are replaced by backward differences. For example, the material balance on carbon monoxide becomes:

$$\frac{1}{\mathcal{A}_{\Delta Z}}\left[(GX_{CO})_{Z+\Delta Z} - (GX_{CO})_Z\right] = c(\mathcal{R}_1)_{Z+\Delta Z} - 2(\mathcal{R}_2)_{Z+\Delta Z} \qquad (4\text{-}35)$$

Similar equations can be written for the remaining differential equations, which, in conjunction with relations 4-13, 4-14, 4-31, and 4-34, represent a complete set of simulation equations for combustion. Thus, given the flow rate, temperature and composition of the gas at position Z, these simultaneous, nonlinear, algebraic equations can be solved for the flow rate, temperature and composition of the gas at position $Z+\Delta Z$. (The well-known Newton-Raphson method is used.) This integration proeeeds step-by-step down the entire length of the combustor. The mole fraction of nitric oxide at each point along the flame is determined by similarly backward differencing equation 4-29 and solving the resulting quadratic in X_{NO}. The flow rate, temperature, and oxygen and nitrogen mole fractions previously computed from the combustion calculations are used in this computation. The corresponding equilibrium value of X_{NO} is also computed by setting the left-hand-side of 4-29 to zero.

This calculation scheme is altered slightly with respect to the heat balance 4-30 in two special cases. When the gas temperature profile has been specified, equation 4-30 is deleted entirely from the set of equations to be solved. Also, when the quench rate option is used, equation 4-32 replaces 4-30 for determination of the gas temperature. To simplify calculations, this equation is forward differenced, so that the temperature at position $Z+\Delta Z$ is immediately determined from:

$$\frac{1}{\alpha\,\Delta Z}\left(T_{Z+\Delta Z} - T_Z\right) = \frac{QR}{(G/\rho)_Z} \qquad (4\text{-}36)$$

The use of 4-36 depends upon the availability of an inlet combustion temperature $T_{Z=0^+}$ (just inside the flame) to get the calculations started. This temperature is obtained by including the heat balance 4-30 with $QR = 0$ (an adiabatic calculation) for the initial integration step. For maximum realism, the adiabatic calculation is continued along the flame until 95% of the theoretical adiabatic flame temperature (previously computed in the model) has been reached. At this point the heat balance equation is replaced by the quench rate equation 4-36 for the remainder of the combustion zone. If there is secondary injection of gas, the adiabatic calculation is made at each injection point, but is immediately replaced by 4-36 for all subsequent integration steps.

The reasons for using an implicit, rather than an explicit (forward differencing), integration scheme, are two-fold:

(a) The explicit scheme is subject to the so-called "ignition" problem. Since reaction rates are extremely low at the relatively low feed inlet temperatures, the explicit integration will never reach the ignition temperature needed for combustion. Furthermore, if there is no H_2O in the inlet feed mixture, the combustion reactions cannot occur due to the $(P X_{H_2O})^{\gamma}$ terms in 4-13 and 4-14. The implicit method is not subject to these types of ignition problems, since the resulting equations are very similar to those for a stirred tank.

(b) The implicit method is much more stable than the explicit one. The explicit method may "fall apart" if the step size is made too large. Furthermore, for a given step size, the implicit scheme is the more accurate one. Conversely, an implicit integration may employ a larger step size (although with a longer calculation time) than an explicit integration.

4.3.2. Results of Mathematical Model Calculations

The computer program calculations performed to date fall into three categories:

(a) Initial calculations on the single stage combustion of methane, at arbitrary, constant quenching rates, varying the amount of excess air. These cases were designed to test the model, and define its sensitivity to input parameters.

(b) Calculations of NO formation in methane combustion, at variable quenching rates. The amount of excess air, and the preheat temperature of the fuel/air mixture were varied. These calculations are more realistic than the first set, insofar that the net rate of heat removal (quenching rate) varies with the temperature of the gases at different points of the furnace.

In addition to methane-air combustion studies, a few cases were included with "oxygen-enriched air" firing, to test the technical feasibility of this approach under idealized conditions, i.e., for a fuel containing no nitrogen.

(c) The last set of calculations were made using a "realistic" quenching rate, i.e., a temperature-residence time profile which is representative of power plant furnace operations. In addition to studying the effect of excess air or NO_x formation, two-stage combustion and flue gas recirculation processes also were simulated.

All of the mathematical model calculations were made on the basis of a nominal 500 MW gas-fired boiler furnace operation, using the following parameters:

A. Methane fuel/oxidizer feed premixed before combustion. Methane feed rate constant = 1000 g. moles/sec.

B. Cross-sectional area of furnace = 1320 ft^2; perimeter of square furnace duct = 142.2 ft.

C. For all computer cases, temperature and concentration (CH_4, CO, CO_2, H_2O, N_2, O_2, NO) profiles were calculated as a function of linear distance from the point of fresh, premixed feed injection.

4.3.2.1 NO Formation at Constant Quenching Rates

The data obtained at constant, high quenching rates of -2000, -10,000, and -50,000°K/sec., are summarized in Table 4-1. Excess air levels of -10%, 5%, 10%, and 50% were used, at a constant feed inlet temperature of 500°K.

The results of these calculations show the following key features:

Table 4-1

Summary of NO Formation Mathematical Model Calculations(1)

(Constant Quenching Rates)

Case No.	Excess Air, %	Quenching Rate, °K/sec	Total Inlet Flow Rate, g moles/sec	Inlet Gas Temp., °K	Furnace Length ft	NO Conc. at Outlet, ppm	NO eq. at Outlet, ppm(2)	Outlet Temp., °K	Adiabatic Flame Temp., °K(3)
1-1	-10	-10,000	9,568	500	4.70	0.0007	4×10^{-7}	1600	(4)
1-2	-10	-50,000	9,568	500	0.94	0.0047	3×10^{-7}	1600	(4)
1-3	-10	- 2,000	9,568	500	23.50	0.00009	4×10^{-7}	1600	(4)
4-1	5	-10,000	11,000	500	3.70	36	412	1600	2392
4-2	5	- 2,000	11,000	500	18.50	174	412	1600	2392
4-3	5	-50,000	11,000	500	0.74	8	412	1600	2392
2-1	10	-10,000	11,472	500	2.20	18	755	1669	2326
2-2	10	-50,000	11,472	500	0.44	4	788	1679	2326
2-3	10	- 2,000	11,472	500	11.00	88	748	1666	2326
3-1	50	-10,000	15,280	500	1.70	0.07	1,118	1600	(4)
3-2	50	-50,000	15,280	500	0.34	0.02	1,118	1600	(4)
3-3	50	- 2,000	15,280	500	8.50	0.33	1,118	1600	(4)

---

(1) **Basis**: Methane fuel/air premixed before combustion; methane flow rate constant = 1000 g moles/sec (fresh feed); single burner, single stage combustor; cross-sectional area of combustor = 1,320 ft^2; perimeter of combustor duct = 145.2 ft.

(2) Calculated from $N_2 + O_2 \rightleftharpoons 2NO$ equilibrium, at combustor outlet temperature.

(3) Adiabatic equilibrium flame temperature corresponding to combustion of specified feed mixture.

(4) Not calculated by computer program.

Table 4-2

Summary of NO Formation Mathematical Model Calculations[1]

(Variable Quenching Rates)

Case No.	Excess Air, %	Quenching Rate Profile No.[2]	Total Inlet Flow Rate g moles/sec	Inlet Gas Temp., °K	Final NO Conc.[3] ppm	NO eq. Conc. at Final Temp.[3,4] ppm	Final Temp.,[3] °K	Adiabatic Flame Temp.,[5] °K
11-1	0	2	10,520	533	75	74	1600	2490
11-2	0	3	10,520	533	52	74	1600	2490
11-3	0	4	10,520	533	49	78	1612	2490
11-4	0	5	10,520	533	64	75	1603	2490
11-5	0	2	10,520	589	117	68	1600	2533
11-6	0	4	10,520	478	15	61	1612	2449
11-7	0	2	10,520	478	127	58	1600	2449
11-8	0	4	10,520	589	102	72	1612	2533
12-1	5	2	11,000	533	178	414	1600	2417
12-2	5	3	11,000	533	109	414	1600	2417
12-3	5	4	11,000	533	91	436	1612	2417
12-4	5	5	11,000	533	117	419	1603	2417
12-5	5	2	11,000	589	402	413	1600	2460
12-6	5	4	11,000	478	31	437	1612	2376
12-7	5	2	11,000	478	73	415	1600	2376
12-8	5	4	11,000	589	255	435	1612	2460
13-1	10	2	11,472	533	99	571	1600	2350
13-2	10	3	11,472	533	56	571	1600	2350
13-3	10	4	11,472	533	42	601	1612	2350
13-4	10	5	11,472	533	53	579	1603	2350
13-5	10	2	11,472	478	36	569	1600	2309
13-6	10	4	11,472	589	126	601	1612	(6)
13-7	10	2	11,472	589	245	571	1600	(6)
13-8	10	4	11,472	478	13	599	1612	2309

---

(1) Basis: Methane fuel/air premixed before combustion; methane flow rate constant = 1000 g moles/sec; single burner, single stage combustor; cross-sectional area of combustor = 1320 ft^2; perimeter of combustor duct = 145.2 ft.

(2) Quenching rate profile numbers correspond to those listed in Figure 4-6: $dT/dt = A + BT_{°K} + CT^{2}_{°K}$, °K/sec.

(3) Computer program "instructed" not to carry out calculations below 1600°K combustor gas temperature.

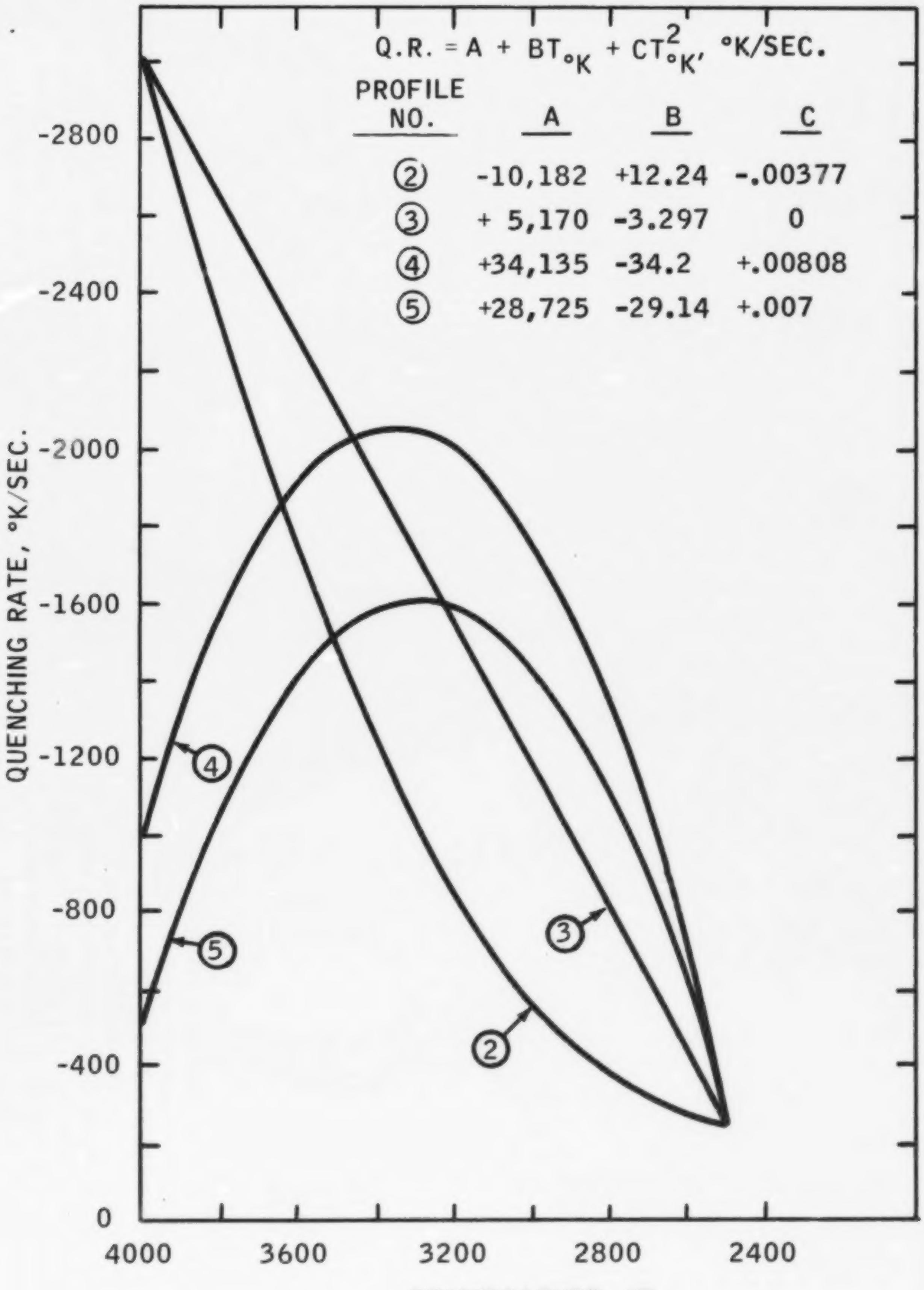
(4) Calculated from $N_2 + O_2 \rightleftharpoons 2NO$ equilibrium, corresponding to final combustor gas temperature.

(5) Adiabatic equilibrium flame temperature corresponding to combustion of specified feed mixture.

(6) Not calculated by computer program.

Figure 4-6

QUENCHING RATE PROFILES



$Q.R. = A + BT_{°K} + CT^2_{°K}$, °K/SEC.

PROFILE NO.	A	B	C
②	-10,182	+12.24	-.00377
③	+ 5,170	-3.297	0
④	+34,135	-34.2	+.00808
⑤	+28,725	-29.14	+.007

A. The model predicts essentially no NO formation at 10% below stoichiometric air requirement. This is not surprising in view of the form of rate expressions used. Both the methane combustion rate expression, and the Zeldovich-type NO kinetics are strictly applicable to fuel-lean conditions only.

B. The assumed constant quenching rates of -2000 to -50,000°K/sec. are unrealistically high for stationary combustion processes. Consequently, the calculated levels of NO formed are much too low, for most cases orders of magnitude below the equilibrium values corresponding to the final temperatures. Nevertheless, the directional effects shown for the combustion variables are meaningful, as discussed below.

C. The level of NO formed increases with decreasing quenching rates. In other words, if the time-temperature profile allows the combustion gases a longer residence time at higher temperatures, higher NO emissions result.

D. The effect of excess air is the same as one would expect for an idealized model in which combustion takes place without mixing limitations. The NO level at quenching rates of -2000°K/sec. and -10,000°K/sec. increases with increasing excess air from 5 to 50%. For the highest quenching rate, -50,000°K/sec., the NO concentration reaches a maximum at 5% excess air (a low value of 8 ppm), indicating the interaction of combustion and NO kinetics with heat removal rates.

4.3.2.2 NO Formation at Variable Quenching Rates

Three levels of excess air operation, 0%, 5%, and 10% were used for computer model calculations at variable quenching rates. Fuel/air inlet temperatures were varied between 400°F and 600°F (478°K and 589°K). The variable quench rates selected are shown graphically in Figure 4-6. These quenching rates have been fitted algebraically in the form:

$$\text{Quenching Rate } \frac{(dT)}{(dt)} = A + BT_{°K} + CT^2_{°K},\ °\text{K/sec.} \qquad (4\text{-}33)$$

In these calculations, the objective was to test the mathematical model at variable quenching rates over a broad range, without attempting to simulate realistic conditions. Of the four quenching rate profiles shown in Figure 4-6, only Q.R. Profile No. 2 may be regarded as typical of the general temperature-time history of combustion gases. However, even this profile operates at unrealistically high quenching rates for power plant furnaces. The computer calculations corresponding to these cases are summarized in Table 4-2. Selected NO-temperature profiles at 0%, 5% and 10% excess air levels are presented in Figures 4-7, 4-8 and 4-9. The major trends indicated by this set of calculations are as follows:

Figure 4-7

NO-TEMPERATURE PROFILES
0% EXCESS AIR

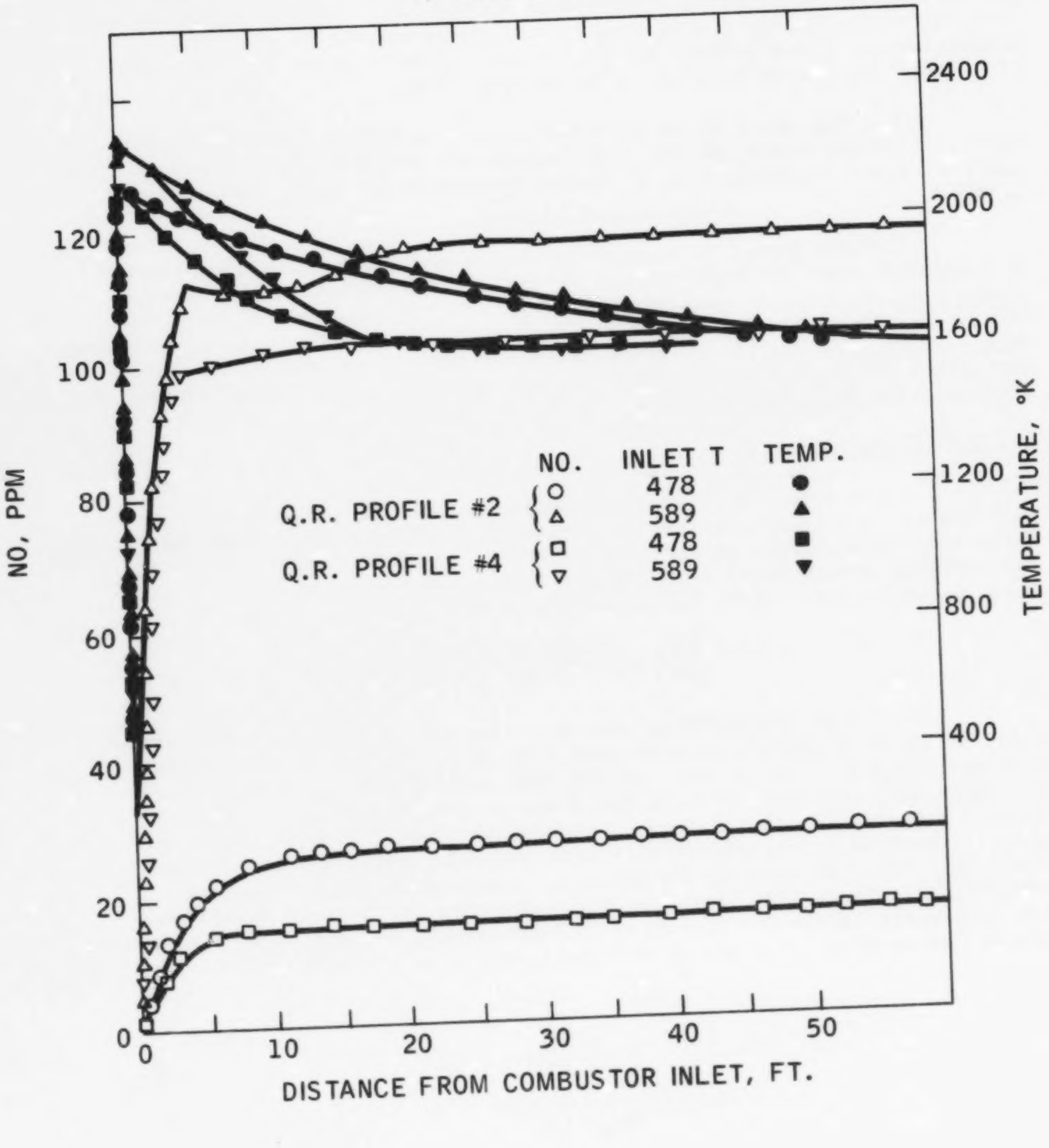
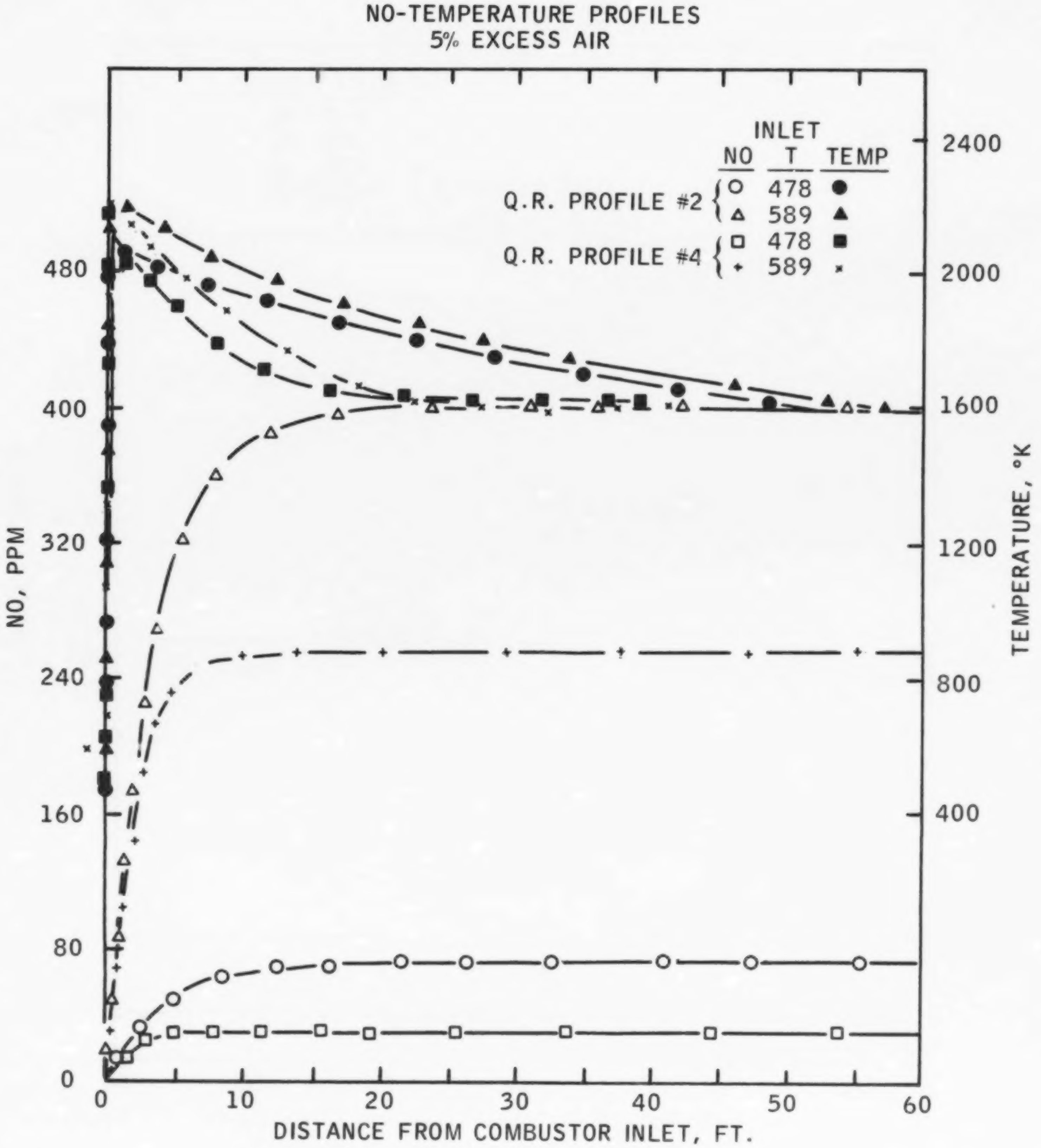


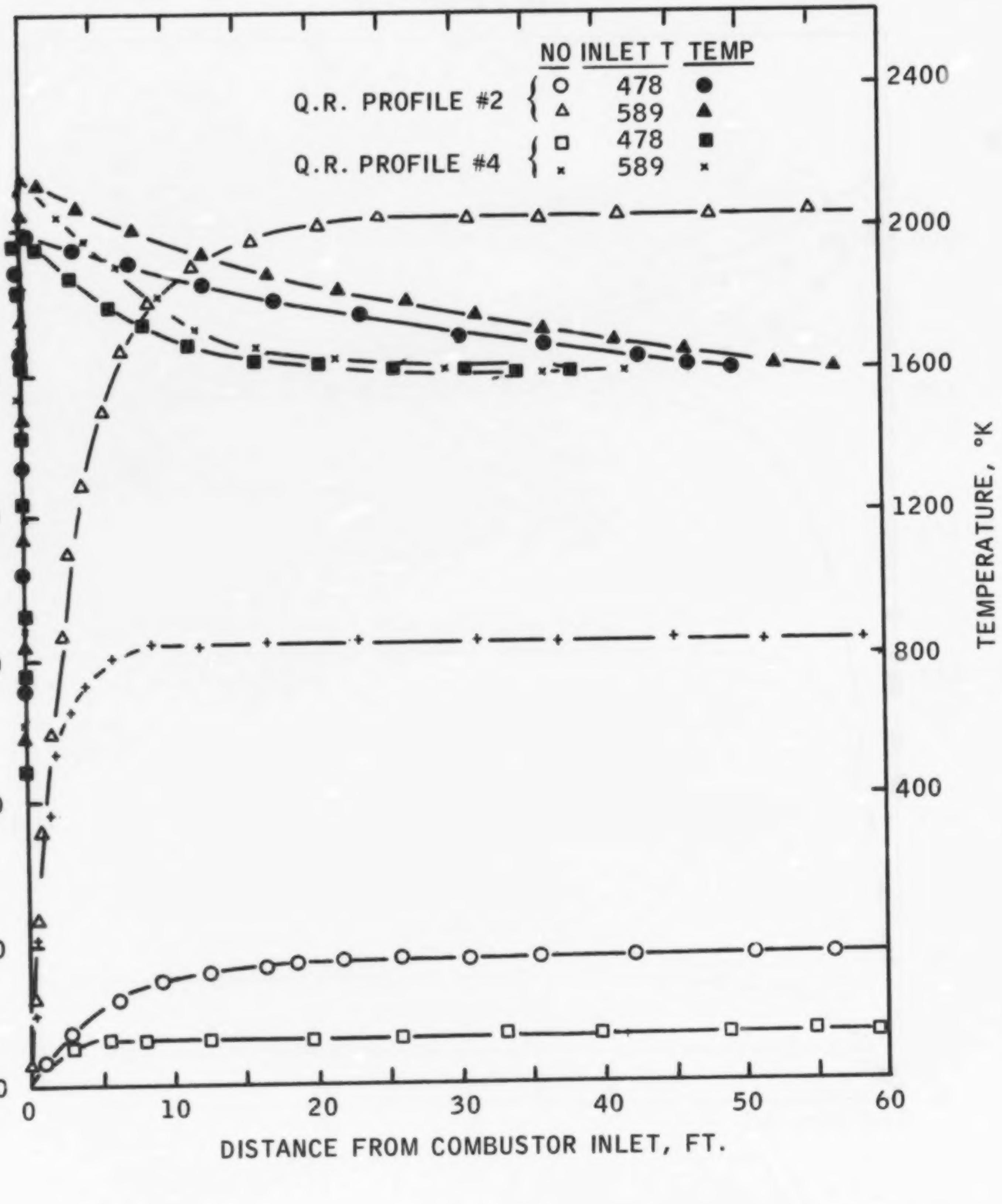
Figure 4-3



NO-TEMPERATURE PROFILES
5% EXCESS AIR

Figure 4-9

NO-TEMPERATURE PROFILES
10% EXCESS AIR



A. Minimum NO levels are found at 0% excess air. The maximum occurs (under otherwise identical conditions) at 5% excess air, while NO levels drop off at 10% excess air. This is due to the idealized nature of the model, which does not take into account mixing limitations.

B. Preheat temperature has a profound effect on peak flue temperatures, and consequently on NO formation. Both peak temperatures and NO levels increase with increasing preheat temperatures.

C. Of the somewhat arbitrary quench rate profiles used, quench rate profile No. 2, which produces the slowest rate of quenching, gives the highest NO levels, as anticipated.

4.3.2.3. NO Formation in Combustion with Oxygen

One approach which has been considered for the control of NO_x emissions from fossil fuel combustion processes is firing with enriched air ("pure" oxygen). Apart from the potential economical limitations for this approach, it was felt on a qualitative basis that the very high flame temperatures reached with enriched air firing would more than offset the deficiency of nitrogen.

To evaluate the possibility of using oxygen (containing only impurity levels of nitrogen) as the oxidizer, a series of cases were calculated using the NO formation model for methane combustion. Based on the JANAF Thermochemical Tables, the adiabatic flame temperature was estimated to be 3213°K for methane combustion with pure oxygen under stoichiometric conditions. Small deviations from this theoretical value were neglected for the computer cases. It was assumed that the actual flame temperature would reach 95% of the adiabatic temperature (as discussed in Section 4.3.1), then quenching rate profile No. 2, shown in Figure 4-6, was applied to develop temperature and concentration profiles for the furnace.

Results of the mathematical model calculations for oxygen firing are summarized in Table 4-3. Two levels of excess oxygen, 1% and 5% were used, assuming that the oxygen was 95, 99, and 99.9% pure, respectively.

As expected, the results in Table 4-3 show increasing NO concentrations with increasing excess oxygen. Also, the NO concentrations increase with decreasing purity of the oxygen stream. However, the remarkable conclusion is that even with 99.9% pure oxygen, NO emissions of 148 ppm and 325 ppm are reached at excess oxygen levels of 1% and 5%, respectively. If the oxygen stream contains 1% N_2 as an impurity, the model predicts NO emissions of 373 ppm and 819 ppm at the above excess oxygen levels. As shown in Table 4-2, the model predicts NO emissions of about 400 ppm with QR profile No. 2, at 5% excess air.

Based on these calculations, it is concluded that fossil fuel combustion with oxygen enriched air is technically unattractive, even for gas-fired installations. The situation would become even worse for fuel oil and coal firing, as these fuels contain chemically bound nitrogen, which is readily oxidized into NO_x.

Table 4-3

Summary of NO Mathematical Model Calculations for Firing with Oxygen (1)

Case No.	% Excess O_2	% O_2 in O_2/N_2 Feed	Peak NO Conc.(2) ppm	Final NO Conc.(2) ppm	Equilibrium NO Conc. at Outlet(3) ppm
22-1	1	95	1817	682	76
22-2	1	99	778	373	34
22-3	1	99.9	202	148	11
24-1	5	95	3965	1482	166
24-2	5	99	1707	819	75
24-3	5	99.9	444	325	24
26-1	1	95	1859	582	13

---

(1) Basis: Single stage, single burner furnace.
Methane feed rate constant = 1000 g. moles/sec.
Furance cross-sectional area = 1320 ft^2 furnace duct perimeter = 142.5 ft.
Furnace length = 50 ft.

(2) Calculated using quench rate profile No. 2: $dT/dt = -10{,}182 + 12.24\, T_{°K} - 0.00377\, T^2_{°K}$.

(3) Calculated for $N_2 + O_2 \rightleftharpoons 2\,NO$ equilibrium corresponding to furnace exit conditions.

4.3.2.4 NO Formation at Realistic Quenching Rates - Simulation of Two-Stage Combustion and Flue Gas Recirculation

In power plant boiler furnaces, essentially all the heat is removed from the combustion gases via radiation, up to the superheater (4-36). A reasonable range of quenching rates under practical conditions is between about -1500°K/sec. (4-37) and -250°K/sec. We have selected a quenching rate profile, designated as Profile No. 6, in which dT/dt varies from -1425°K/sec. at 2400°K (3860°F) to -278°K/sec. at 1600°K (2420°F). Between these limits, the quenching rate is proportional to the fourth power of the absolute temperature. Quenching rate profile No. 6, fitted again in the quadratic form, is shown in Figure 4-9.

Using Q.R. profile No. 6, and a constant preheat temperature of 533°K (500°F), the rate of NO formation was calculated under the following conditions:

- Single stage combustion, excess air levels of 0%, 5%, and 10%.

- Two-stage combustion, overall excess air levels of 5 and 10%, first-stage excess air 0%. (It was necessary to simulate two-stage combustion by operating at stoichiometric conditions in the first stage, because the present version of the model cannot treat substoichiometric combustion cases realistically.) Secondary injection of air was made at 5, 10, and 20 ft., respectively, downstream of the location of primary feed injection.

- Flue gas recirculation back into the primary flame zone was simulated at excess air levels of 5% and 10%. Recirculation rates of 10% and 50% were tested.

The results of these computer model cases are summarized in Table 4-4. The highlights of the conclusions reached are as follows:

A. Low excess air firing (i.e. stoichiometric air supply) results in low NO_x emissions. The peak concentrations of NO increase in the order of 468 ppm at 0%, 1586 ppm at 5%, and 1178 ppm at 10% excess air. The corresponding final concentrations of NO increase in the order of 259 ppm at 0%, 1192 ppm at 5%, and 1178 ppm at 10% excess air. As discussed earlier, this idealized, premixed model predicts maximum NO concentrations at about 5% excess air.

It is interesting to note that the model predictions are in fair agreement with actual measured emissions from large, gas fired power plants. Thus, the simulation obtained with this first-generation model appears to be quite satisfactory. Calculated temperature and NO concentration profiles corresponding to the above cases are shown in Figure 4-10.

Figure 4-10

"REALISTIC" QUENCHING RATE PROFILE

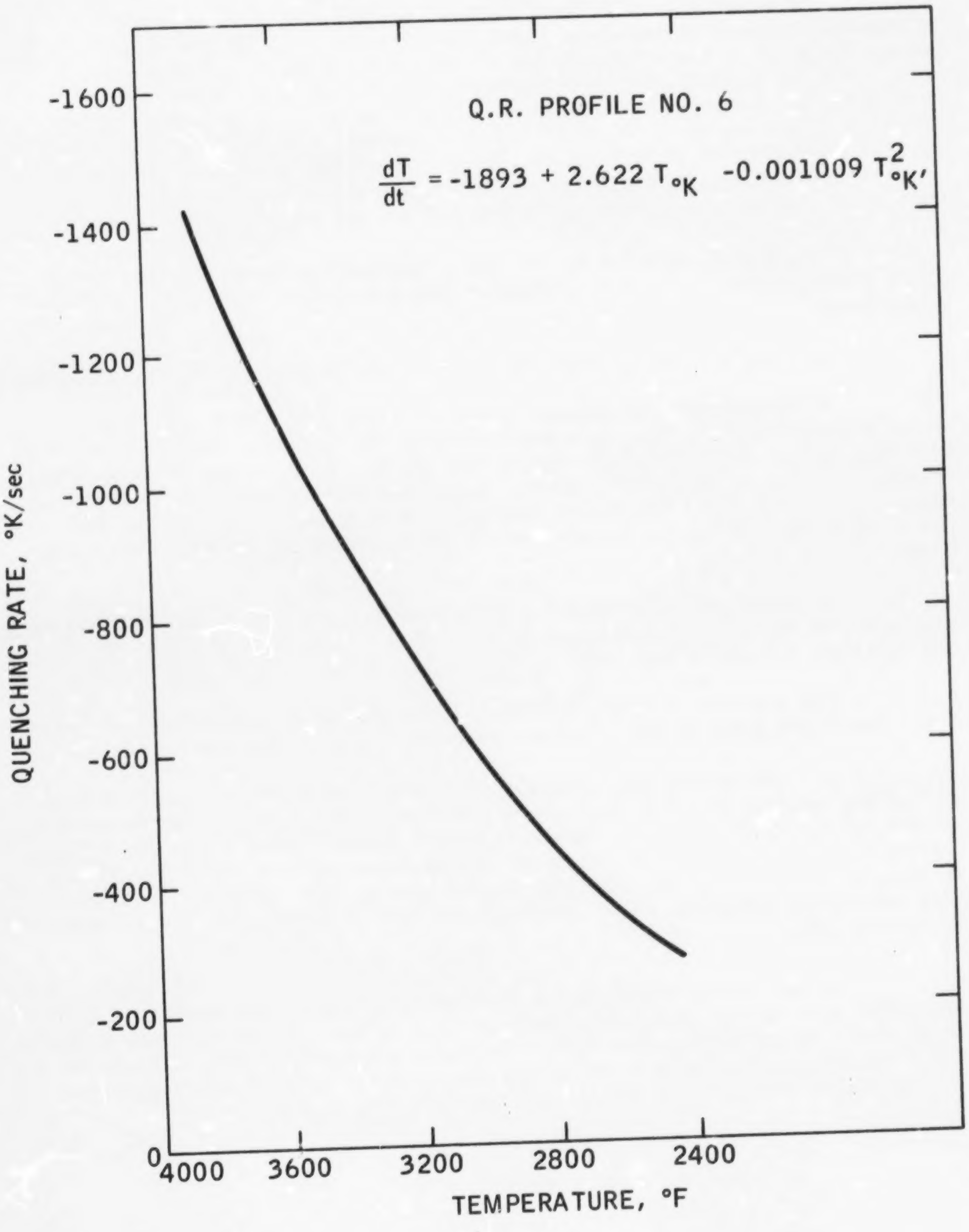


Table 4-4

Summary of NO Formation Mathematical Model Calculations - "Realistic" Quenching Rates(1,5)

Case No.	Stages	Distance of Secondary Injection Point, ft	Recirculation Rate, %	NO_x in Recirculated Flue Gas (Total Feed) ppm	Stage 1(2) Flow Rate g Moles/Sec	Air Injected in Stage 2(3) g Moles/Sec	Inlet Gas Temp., Stage 1 °K	Inlet Gas Temp., Stage 2 °K	Overall Excess Air, %	First Stage Excess Air, %	Adiabatic Flame Temperature °K	Peak Temp. Calculated °K	Peak NO ppm	Final NO ppm	NO Equilibrium(4) at Outlet ppm
30-1	1	--	0	--	10,520	--	533	--	0	--	2,490	2,413	468	259	129
30-2	1	--	0	--	10,520	--	589	--	0	--	2,533	2,470	583	268	134
30-4	1	--	0	--	11,000	--	533	--	5	--	2,417	2,346	1,586	1,192	767
30-5	1	--	0	--	11,000	--	589	--	5	--	2,460	2,351	1,479	1,146	760
30-7	1	--	0	--	11,472	--	533	--	10	--	2,350	2,278	1,178	1,178	1,008
30-9	1	--	0	--	11,472	--	589	--	10	--	2,393	2,277	1,176	1,176	1,005
31-1	2	5	0	--	10,520	952	533	533	10	0	2,490	2,413	815	815	982
31-2	2	10	0	--	10,520	952	533	533	10	0	2,490	2,413	499	499	952
31-3	2	20	0	--	10,520	952	533	533	10	0	2,490	2,413	468	240	894
32-1	2	5	0	--	10,520	480	533	533	5	0	2,490	2,413	814	814	717
32-2	2	10	0	--	10,520	480	533	533	5	0	2,490	2,413	579	579	746
32-3	2	20	0	--	10,520	480	533	533	5	0	2,490	2,413	468	260	727
34-1	1	--	10	99(9)	12,619	--	493	--	10	--	2,167	2,076	119	119	794
34-2	1	--	10	178 (16)	12,100	--	493	--	5	--	2,228	2,137	206	206	617
34-3	1	--	50	178 (53)	16,500	--	474	--	5	--	1,968	1,876	56	56	467

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(1) Basis: Methane/air premixed before combustion; methane flow rate constant = 1000 g moles/sec; cross-sectional area of combustor = 1320 ft^2; perimeter of combustor duct = 145.2 ft; combustor length = 40 ft.

(2) Stage 1 Compositions

	Mole Fraction
CH_4	0.0950
O_2	0.1901
N_2	0.7149

(3) Stage 2 Compositions

	Mole Fraction
O_2	0.21
N_2	0.79

(4) Calculated from $N_2 + O_2 \rightleftharpoons 2NO$ equilibrium, corresponding to final combustor gas temperature.

(5) Quenching rate Profile No. 6: $dT/dt = -1{,}893 + 2.622\ T_{°K} - 0.001009\ T^2_{°K}$, °K/sec.

Figure 4-11

NO-TEMPERATURE PROFILES
EFFECT OF EXCESS AIR

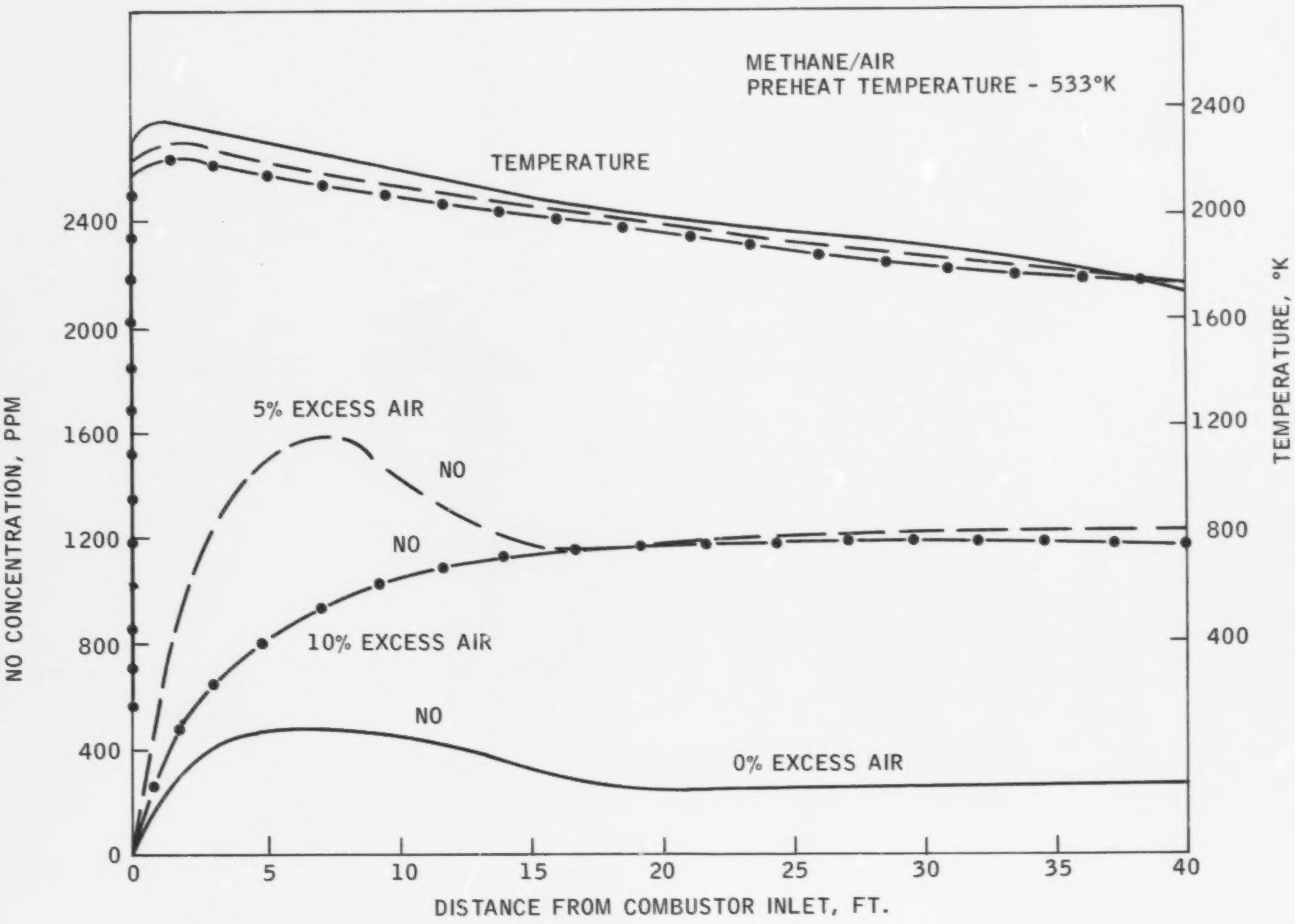


Figure 4-12

NO-TEMPERATURE PROFILES
EFFECT OF TWO-STAGE COMBUSTION

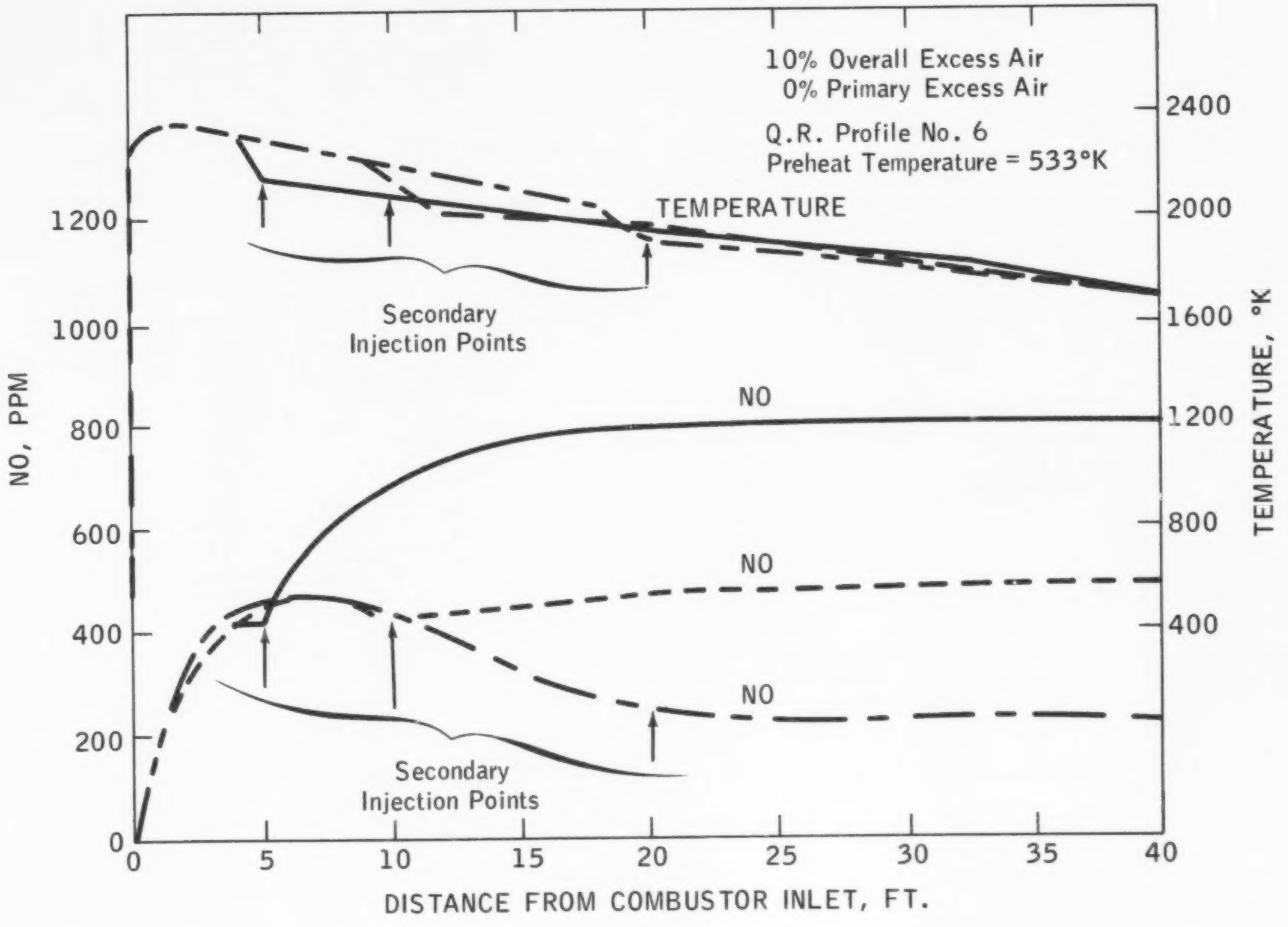


Table 4-13

NO TEMPERATURE PROFILES
EFFECT OF FLUE GAS RECIRCULATION

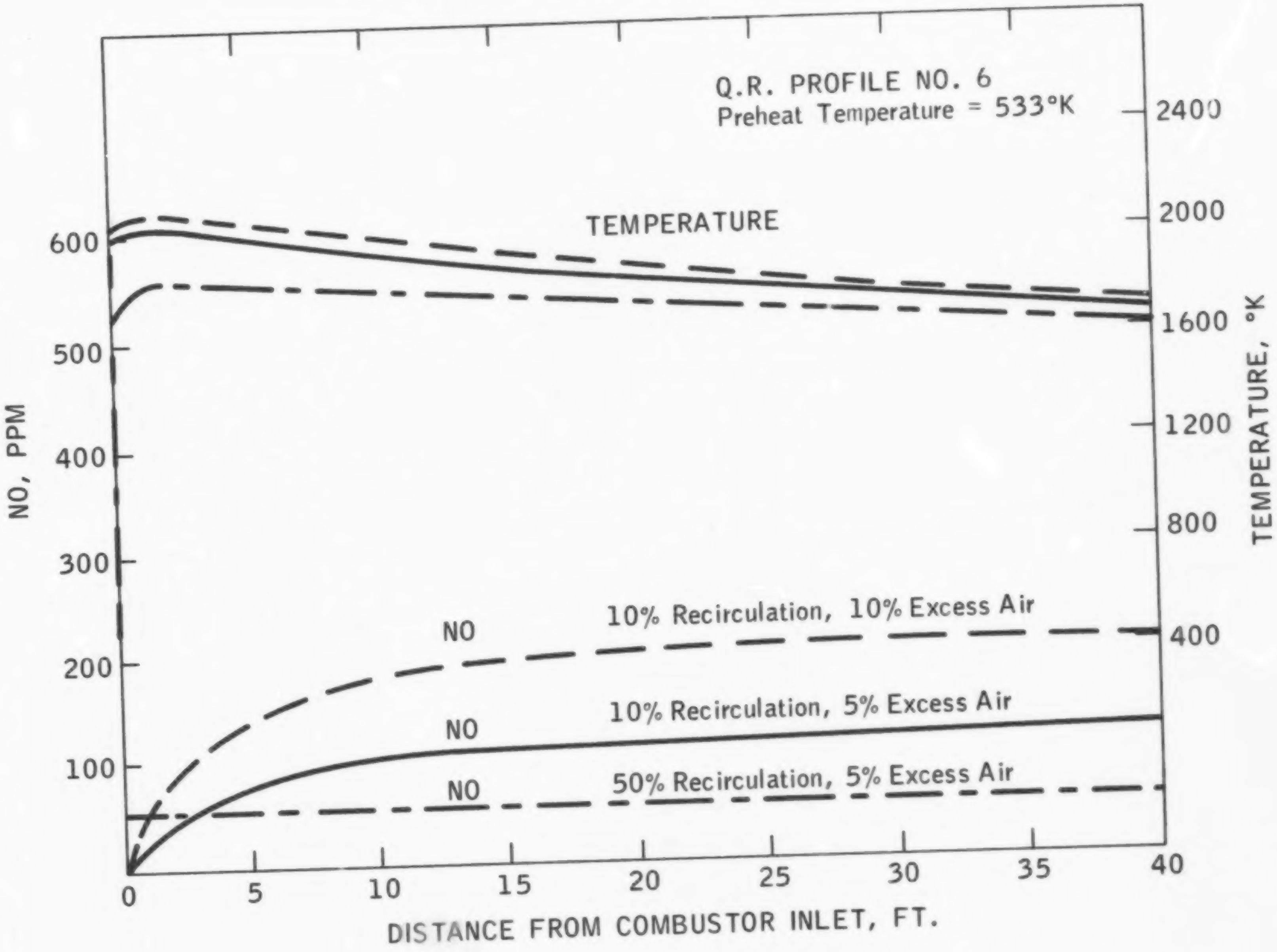
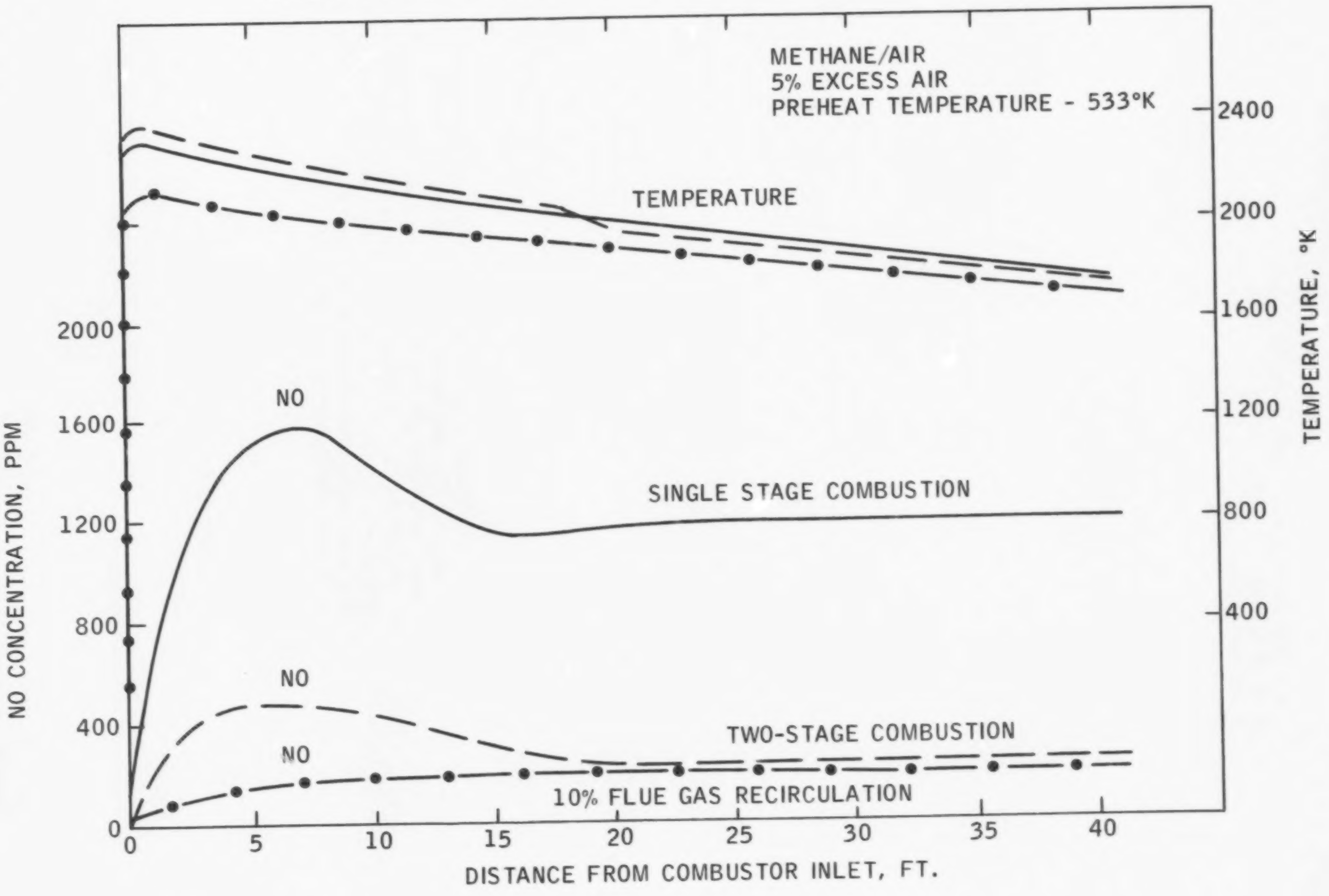


Figure 4-14

NO-TEMPERATURE PROFILES
EFFECTS OF TWO-STAGE COMBUSTION AND FLUE GAS RECIRCULATION



B. The directional effect of two-stage combustion is correctly predicted by the model. As expected, the model predicts decreasing levels of NO_x emissions as the distance between primary and secondary injection points is increased. This effect is due to the cooling of combustion gases with distance. In other words, the farther the secondary injection point is, the lower the temperature of the combustion gases at that point, hence, lower concentrations of NO result.

With secondary injection at 5, 10 and 20 ft., final NO concentrations of 815, 499, and 240 ppm, respectively, are predicted at an overall excess air level of 10%. These concentrations correspond to reductions in NO_x emissions of 30%, 60%, and 80%. Thus, the model predictions are directly in line with operating experience using the two-stage combustion technique. These model predictions for two-stage combustion are shown in Figure 4-11.

C. The model also predicts correctly the directional effect of flue gas recirculation. As discussed in Sections 4.1 and 4.2, lowering the primary flame temperature can drastically reduce NO_x emissions. This effect is accomplished by flue gas recirculation, primarily because of the thermal dilution of the flame (4-13).

As shown in Table 4-4, the mathematical model predicts NO_x reductions as high as 90%, with 10% flue gas recirculation. Flame temperature would be so severely lowered by 50% flue gas recirculation (an impractically high level), that essentially just the recirculated NO "survives" the combustion zone (53 ppm NO in the feed, vs. 56 ppm in the flue gas). The calculated NO and temperature profiles for the flue gas recirculation cases are shown in Figure 4-12. Although these calculations may attribute an excessively high reduction of NO_x *via* recirculation, the predictions are in good directional agreement with experimental data, which will be discussed in Section 4.4.

In Figure 4-13, mathematical model predictions are shown at a constant excess air level of 5%, and preheat temperature of 533°K, for single stage, two-stage, and flue gas recirculation, respectively. This figure clearly shows the powerful potential of combustion modification techniques for NO_x emissions control. It (as well as the data presented before) indicates that our first-generation mathematical model is basically sound, and that with further refinements the model should become capable of quantitative predictions.

4.3.3 Suggested Extensions of NO_x Model

As it stands, the mathematical model is useful for directional predictions of the effects of combustion variables on NO_x emissions. To make the model more sophisticated, and eventually useful for guiding the design of low emission combustion equipment, the following modifications are suggested for the future.

A. Incorporate additional kinetics on fuel combustion and NO formation and decomposition rates. Information at present is sorely lacking on combustion and NO kinetics under fuel rich conditions. As such information becomes available from kinetic studies, it will be possible to model the rate processes affecting NO_x emissions from combustion processes.

In the present version of the model, fuel and CO combustion rates are so fast that at stoichiometric or higher air supply levels, the amounts of unburned fuel and carbon monoxide are calculated to be negligible. More realistic estimates of the rate of oxidation of fuel and carbon monoxide will allow the refinement of the model to reflect slower rates of reaching peak flame temperature, and hence, the competition for oxygen between combustibles and molecular nitrogen even under substoichiometric firing conditions. This type of extension of the model will allow more realistic estimates of the fate of unburned fuel, partially oxygenated hydrocarbons, and carbon monoxide in conjunction with the calculation of NO formation and decomposition rates. Thus, the modeling studies should culminate in realistic assessments of the emissions of all potential pollutant species from fossil fuel combustion processes.

B. Study the effects of mass and heat transport by mixing model simulations. The present model has the basic capability of multiple point injection; the next step should be to simulate the distribution of fuel and air by combining model elements operating under different fuel/air stoichiometric conditions. Internal recirculation may be simulated by withdrawing and reinjecting combustion gases at intermediate points.

C. Extend the model to the combustion of oil droplets and coal particles. These features will require the incorporation of spray droplet size distributions, vaporization and combustion rates for fuel oil sprays, and particle size distributions and burning rate laws for coal particles.

D. Program the model to simulate multiple burner installations. In principle, this is already possible with the present version of the model by multiple injection of fuel and/or air.

E. When reliable data become available on the kinetics of oxidation of chemically bound fuel nitrogen (according to compound type) include these parameters into the mathematical model.

F. Validate and refine the model by comparison with actual NO_x measurements.

4.4 ANALYSIS OF COMBUSTION MODIFICATION TECHNIQUES AND THEIR APPLICABILITY

Modifications to the combustion process, as shown by a number of investigators, can be very effective in reducing NO_x emissions. The more effective combustion control modification techniques have been identified and analyzed relative to their applicability to equipment accounting for the major sources of NO_x emissions. The simplicity of altering operating conditions, or making relatively minor changes in design features potentially offers inexpensive, readily applicable means for control. The extent to which combustion modification techniques can be applied to the large variety of existing stationary equipment remains to be defined. Similarly, the range of NO_x reductions possible in combustion equipment, using the techniques discussed in detail below must be determined. In some installations, perhaps only a 10% reduction in NO_x may be possible while in others a combination of techniques may reduce emissions by as much as 80-90%.

4.4.1 Modification of Operating Conditions

As discussed in Sections 4.1, 4.2, and 4.3, a detailed understanding of the kinetics of NO formation is useful for predicting the success a change in operating conditions will have on NO_x formation and control. Thus, as dictated by kinetics, any change which lowers flame temperature, limits the availability of reactants, oxygen or nitrogen, or a combination of these factors will lower NO_x emissions. The combustion modifications made by changes in operating conditions discussed below, are the ones found to be most effective in the control of NO_x emissions.

4.4.1.1 Low Excess Air Combustion

In most combustion systems a certain amount of excess air is necessary in addition to that required for stoichiometric combustion, to complete combustion within the confines of the combustion chamber. The more efficient the burners are in mixing, the smaller the necessary quantity of excess air. The minimum amount of excess air used in any system is limited by the production of smoke or unburned combustibles ($CO + H_2$). However, further quantities of excess air may be required for the following reasons:

(a) To maintain steam temperature at desired levels.
(b) To prevent damage to refractories or other sensitive parts.
(c) As a means of process control.
(d) To compensate for instrument lag during load swings.
(e) To complete combustion on 1 or 2 burners in a multiple burner installation where air supply is "unbalanced" or not uniform.
(f) Also, a further source may be air which leaks through the furnace casing, or through burners which are out of service.

Generally, the level of excess air used in combustion systems in the United States ranges from a minimum of about 10% to as high as 300 or 400%. Because of the huge quantities of fuels consumed, public utility boilers normally operate at the lower excess air levels, ranging from a minimum of about 10% to a high of 35 to 40% in older installations and averaging perhaps 12 to 15% in "normal" boiler units. Some commercial and industrial boiler installations have the capability of operating at as low as 10% excess air, but the average usually is 15 to 25%, with some older and smaller units operating at 35 to 40%. Excess air levels used in process furnace applications found in industry such as, kilns, glass tanks, refineries, open hearth and heating furnaces, blast furnace stoves, etc., range from a low of perhaps 10% to as high as 50 to 60 percent. In some cases, excess air is varied, as in blast furnace stoves, where excess air is increased during the heating cycle to maintain roof dome refractory temperatures within safe limits. Residential home heating furnaces, because of the unsophisticated design of this type of equipment, operate in the range of 80 to 100% excess air. Gas turbine installations, in order to maintain blade temperatures at prescribed safe limits, use in the neighborhood of 300 to 400% excess air, depending on the manufacturers' design. However, most of the excess air in gas turbine combustors is added as secondary air, at lower temperatures than in the primary combustion zone. Thus, relatively low NO_x emissions result, and are further diluted by the addition of large amounts of excess air.

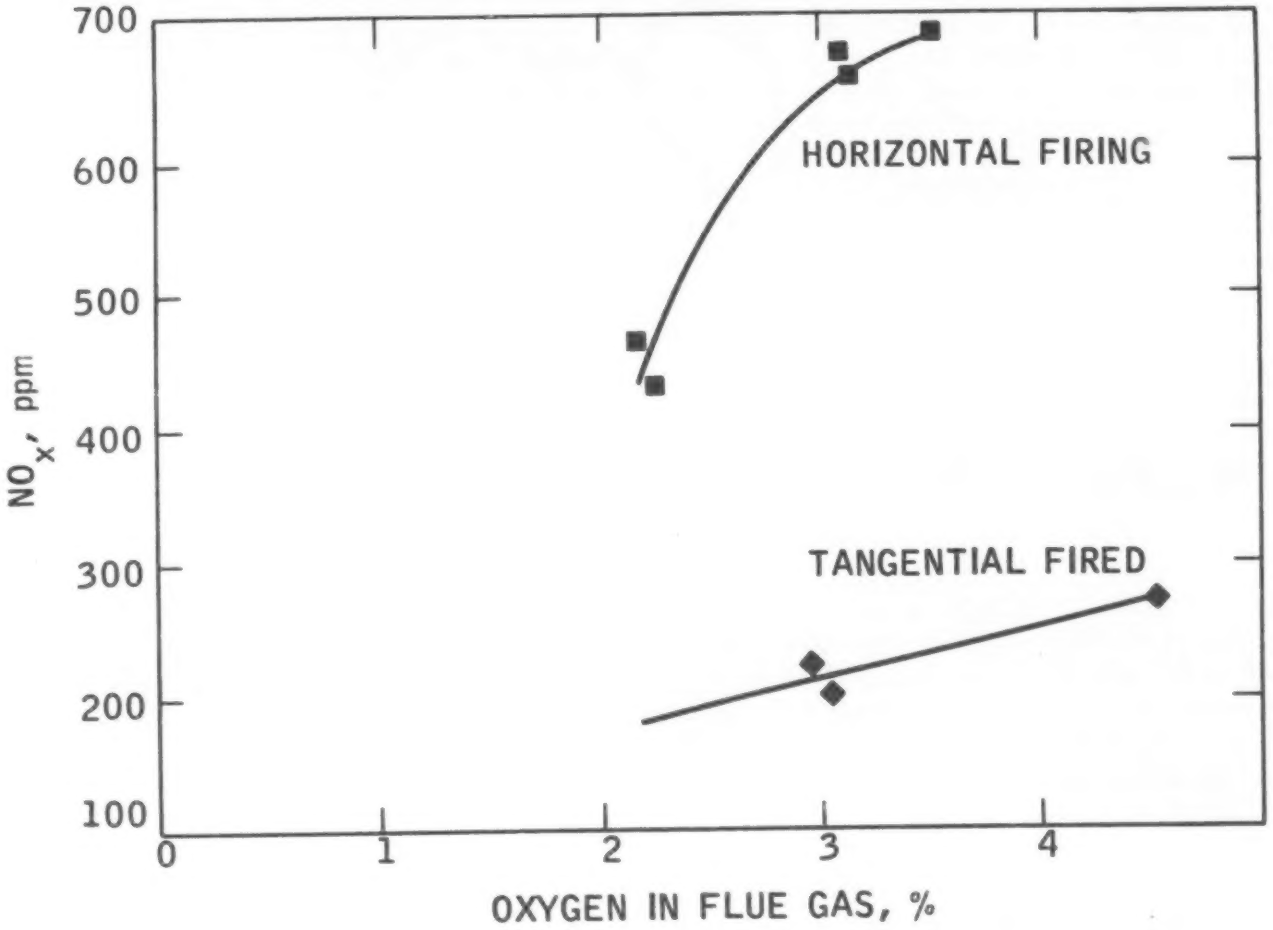
With any fuel the highest efficiency is obtained by using a minimum amount of excess air. However, efficiency alone is not the only, or the principal reason for resorting to low excess air firing. This technique has been developed chiefly to reduce corrosion problems attributed to the oxidation of SO_2 to SO_3 in the combustion of sulfur-containing fuels. Excess air levels of 10 to 15% and higher, as indicated above, are now regarded as representing "high" excess air operation.

In the late 1950's in the United Kingdom "low" excess air boiler operation was explored as a means for overcoming undesirable operating conditions on oil fired boilers (4-38), such as low temperature corrosion and air heater plugging. Later, European boiler operators made further refinements in this type of operation, claiming additional operating advantages, particularly the virtually complete elimination of furnace slagging and heating surface fouling (4-39, 4-40, 4-41). Subsequent studies in a laboratory test furnace (4-42) confirmed that operation at the 3 to 4% excess air level was necessary to realize full benefits. In the early 1960's, the low excess air firing technique was introduced to public utilities in the United States and has now been adopted as regular practice at some oil and gas fired power plants. "Low" excess air firing is now generally regarded as operation below 5 percent excess air.

While theory predicts a reduction of NO_x emissions with lower excess air, actual data are still limited on this type of operation. Investigations by Sensenbaugh and Jonakin (4-43) on oil fired boilers, reported in 1960, showed that NO_x emissions decrease as the oxygen content of the flue gas is reduced even at the higher levels of excess air. This is shown in Figure (4-15) based on Figure 5 of reference (4-43).

Figure 4-15

EFFECT OF EXCESS AIR ON NO_x
EMISSIONS FROM OIL FIRED BOILERS*

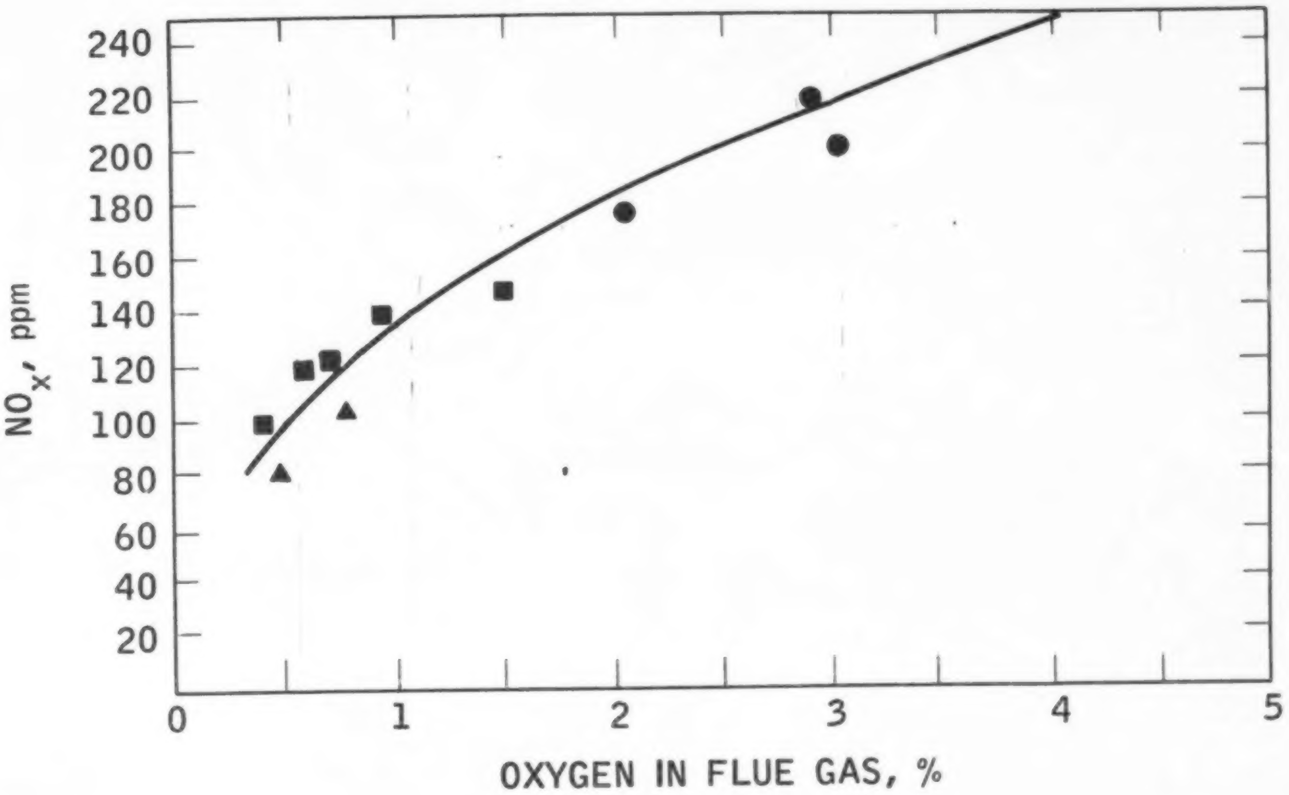


* After Ref. (4-43).

NO_x reductions of 36% in a horizontal oil fired boiler and 28% in a tangentially fired unit were obtained as flue gas oxygen content was decreased from 3.5-4.0% to about 2%. Subsequent investigations at much lower excess air (2-3% excess air, 0.4-0.6% O_2) in oil fired installations indicate that NO_x reductions of up to 63% can be achieved by lowering excess air from 15% to the 2-3% level. Figure 4-16 based on Figure 17 of the Fernandes, Sensenbaugh and Peterson report (4-44) illustrates the magnitude of NO_x reductions possible in oil fired

Figure 4-16

NO_x EMISSIONS FROM OIL FIRED BOILERS AT LOW EXCESS AIR*

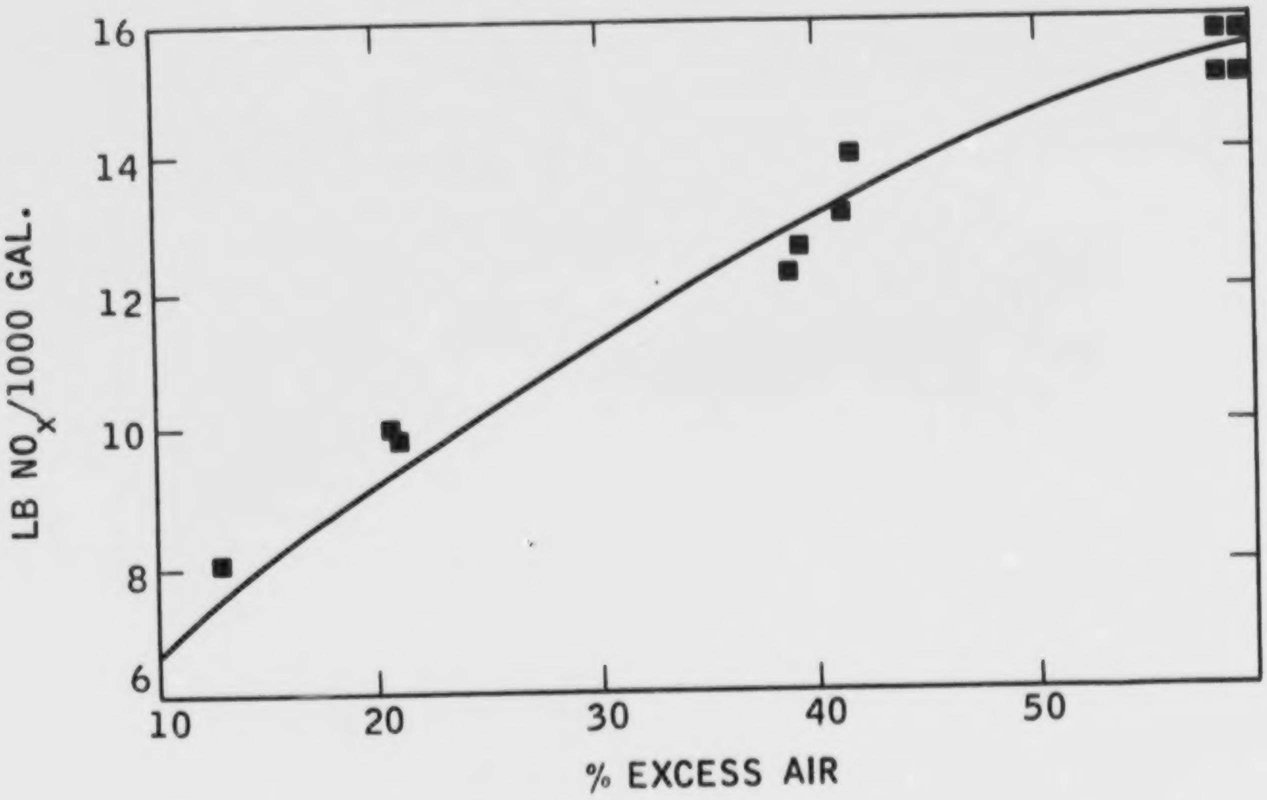


* After Ref. (4-44).

boilers operating at low excess air. Similar effects have been observed in laboratory tests of an oil fired domestic heating installation, (4-45) where the level of excess air is much higher than in the larger utility boilers. Figure 4-17 based on Figure 4 in reference (4-45) shows the effect of excess air on NO_x emissions in this type of equipment.

Figure 4-17

NO_x EMISSIONS FROM DOMESTIC HEATING OIL COMBUSTION*

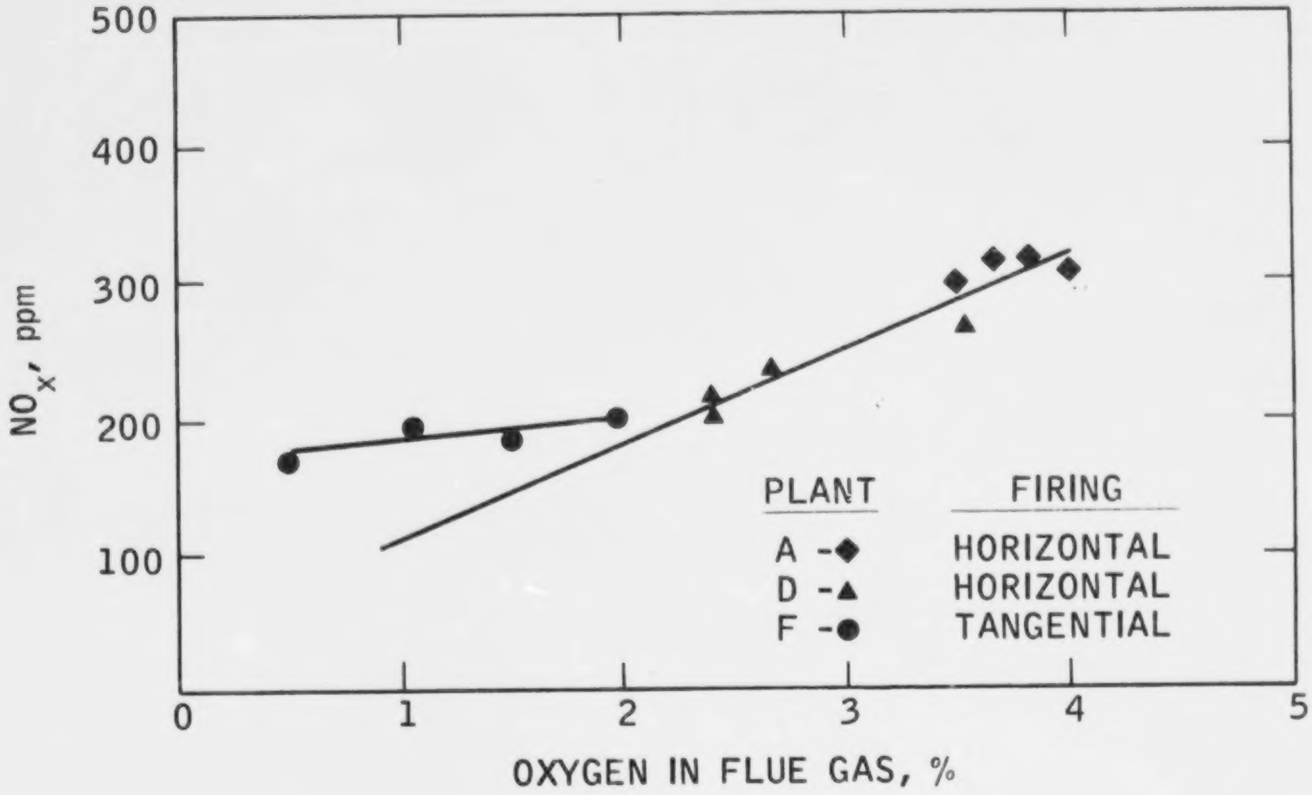


* After Ref. (4-45).

There is relatively little published information on applications of low excess air combustion in gas fired installations. However, the limited available data indicates that NO_x reductions similar to oil firing may be expected with gas firing. For instance, one source of published data, taken at relatively high excess air levels (4-44), provides an indication that similar decreases in NO_x may be expected. Figure 4-18

Figure 4-18

EFFECT OF EXCESS AIR ON
NO_x EMISSIONS FROM GAS FIRED BOILERS*



* After Ref. (4-44).

based on Figure 16, in reference (4-44), shows that this effect is more pronounced in a horizontally fired boiler than in one fired tangentially. Recently obtained unpublished data also demonstrate the favorable effect of low excess air combustion with gas. This information shows that the effect is the same with either type of firing and that decreases in NO_x of up to at least 1/3 can be achieved using the low excess air technique. (4-18)

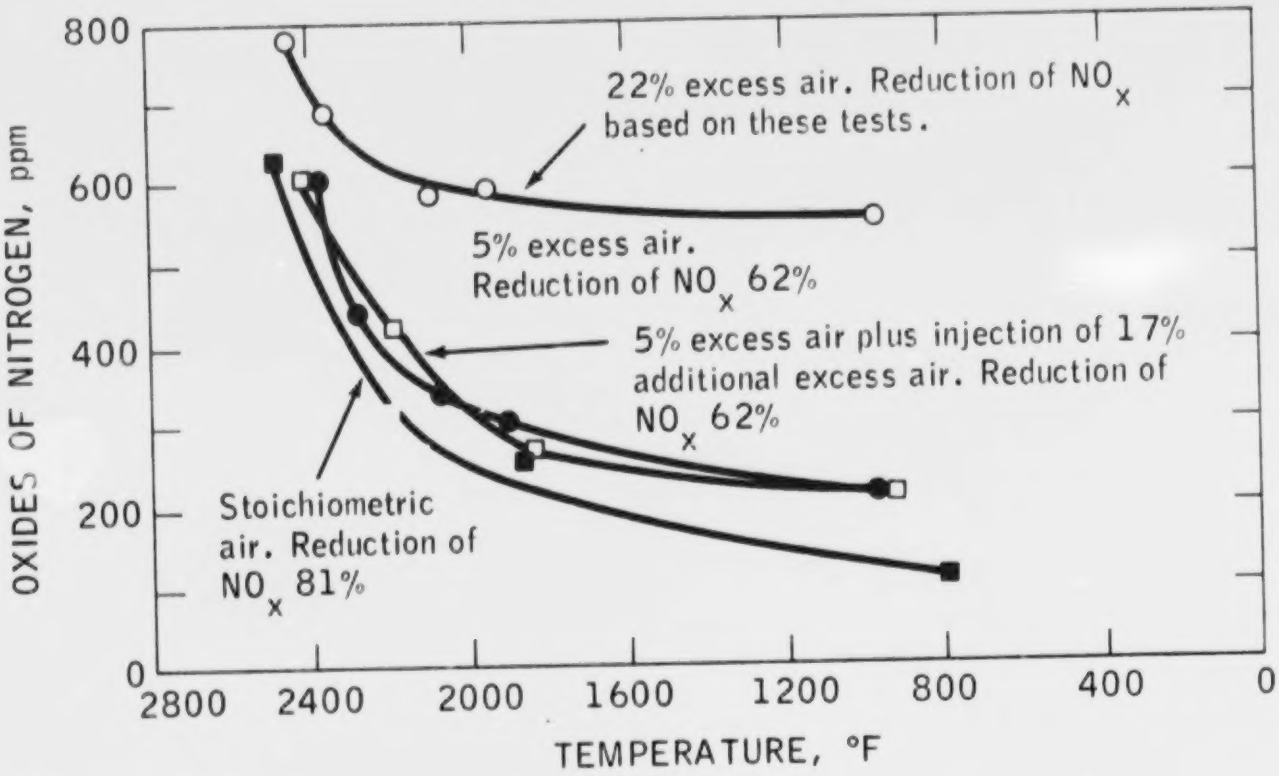
There is little or no published information on applications of low excess air firing principles to commercial pulverized coal installations. Any attempts which may have been made to apply this technique either have not been well documented, or have met with little success. However, investigations in a laboratory test furnace with a single burner (4-14) confirm that NO_x from pulverized coal firing varies in a similar manner with excess air as with oil or gas firing. According to Figure 4-19 based on Figure 4 of reference (4-14), NO_x emissions decreased by 62% at stack temperature conditions of 975°F when excess air was decreased from 22% down to 5 percent. At stoichiometric conditions, NO_x was decreased further, by a total of 81%. These improvements in emissions, however, were accompanied by increases in the carbon content of the fly ash of 13.8 and 42.3 percent, respectively. The conclusion of this study (4-14) was that the concentration of NO_x in the stack gases varied directly with a decrease in excess air (and flame temperature), but that combustion efficiency was adversely affected.

It appears that applications of low excess air combustion to pulverized coal systems will be considerably more difficult than with gas or oil firing. For instance, regulation of coal streams to individual burners to obtain a uniformity of fuel distribution among burners served by a single pulverizer, poses severe problems. In addition to non-uniform fuel distribution between burners and pulverizers, the problem is compounded by further inbalances between primary and secondary air streams. The arrangement for distributing pulverized coal to individual burners also complicates achieving low excess air combustion. However, since the largest quantity of fuel consumed in the U.S. for electricity generation is coal, (mostly pulverized coal) development of this control technique for pulverized coal firing is an important area for future research. The feasibility of low excess air operation in a pulverized coal system, however, remains to be demonstrated.

The potential reduction in NO_x emissions which may be realized via applications of low excess air firing to stationary combustion systems warrants full investigation. Gas and oil fired systems lend themselves to relatively easy conversion, in some cases at very little or no cost as will be discussed in Section 8. Fuel savings resulting from low excess air operation help to defray conversion costs and can effect a net decrease in operating costs. The feasibility of applications of this technique to pulverized coal firing remains to be determined. With all types of firing, the extent of NO_x reductions possible, the cost of conversions, and the applicability to given processes must still be demonstrated.

Figure 4-19

EFFECT OF LOWERING EXCESS AIR AND TWO-STAGE COMBUSTION ON NO_x EMISSION FROM COAL COMBUSTION*



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* After Ref. (4-9)

4.4.1.2 Two-Stage Combustion

In the course of the California investigation in the late 1950's, it was observed (4-46) that delayed mixing of the fuel and air and operation of burners with less than the normal amount of combustion air results in substantial reductions in NO_x emissions. Effective application of these principles led to the development of a two-stage type of burner which is currently being used in a number of Los Angeles County power stations. In this type of burner, about 95% of the stoichiometric air needed for combustion is admitted to the flame through the burner throat. The remainder of the air required for complete combustion is injected through ports above the burner to complete the burnout of the initial combustion phase. Operating under such conditions, reductions of 30% in NO_x emissions were observed, while admission of only 90% of the stoichiometric air into the primary zone resulted in a 47% reduction of NO_x.

This technique has been applied successfully to oil and gas firing, but to our knowledge, no data are available on applications in commercial coal-fired boilers. In laboratory tests of a single burner pulverized coal fired furnace (4-14), it was shown that by supplying 5% excess air to the primary combustion zone and an additional 17% injected just beyond the flame (two-stage combustion), the same 62% reduction in NO_x was obtained as resulted when operating at 105% stoichiometric air. In addition, carbon combustion efficiency was improved over that when only low excess air firing was employed. More important, it was concluded that with this type of operation not only was NO_x reduced substantially but, as the same amount of air is used as in conventional pulverized coal burning plants, no significant change in equipment would be required and the same rate of heat transfer could be expected.

Reports (4-18) have also been received on two large gas fired public utility boilers where a modified or simulated type of two-stage combustion was employed in combination with low excess air firing to reduce NO_x emissions from about 1500 ppm to acceptable levels of less than 200 ppm. The two-stage combustion principle was simulated by cutting the fuel off in top burners, combusting the fuel in the bottom burners at substoichiometric conditions, and using the top burners as air ports to supply air for complete burnout. This modified form of two-stage combustion was found to be very effective, as reductions in NO_x of up to 90% could be achieved. Of particular importance is the fact that this NO_x control was achieved without additional investment cost.

Recent "breakthroughs" in NO_x emission reductions have been reported by the Southern California Edison Company engineers (4-47). These were attributed to "refinements of the two-stage combustion process." No details are available regarding these refinements, but the report significantly emphasizes the importance of the two-stage combustion principle for the control of NO_x emissions.

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* Pacific Gas and Electric Co., Private communication.

The effect of two-stage combustion on NO_x emissions may be explained by a combination of several factors. First, there is a lack of available oxygen for NO_x formation in the first stage operated under sub-stoichiometric air conditons. Second, the flame temperature may be lower in this first stage than in normal combustion. Third, to the degree that heat is removed between stages, the maximum flame temperature in the second stage is lower than for single stage combustion. Fourth, the effective residence time available for NO_x formation at the peak temperatures reached in the second stage may be reduced.

Based on the effects observed with the use of two-stage combustion, it is worthwhile to consider the optimization of this technique for power plant furnaces having a variety of design and operating features. Combinations of two-stage combustion with other combustion modification techniques undoubtedly could lead to even further improvements in NO_x emission control.

4.4.1.3 Flue Gas Recirculation

Flue gas recirculation is a technique which has been applied in specific combustion processes to achieve certain desirable operating conditions. Processes employing this technique provide some means for recycling a portion of the flue gases produced back to the combustion chamber using either forced or natural draft. The effect on combustion conditions depends on the point of injection into the combustion system, and the amount of gas recycled. Flue gas injected into the primary flame zone has the effect of (1) decreasing flame temperature and (2) diluting the combustion air and resultant flue gases. Where flue gas is introduced for boiler tube temperature control, the effect is largely one of dilution. The quantity of gas recirculated is important and has a direct effect on the combustion modifications desired.

In the past 15 to 20 years, flue gas recirculation has frequently been used in large steam boilers as a means of controlling superheat temperature. A Babcock and Wilcox Company publication (Steam, 37th Edition, pages 13-15) states, "the recirculated gas is preferably introduced into the furnace at a location, and in a manner, so that the entering flue gas will reduce the effectiveness of the furnace heat absorption surface, decrease the residence of the hot gas stream in the furnace, and yet not interfere with the process of combustion." In the course of the California Joint Project in 1960-62 (4-48), the effect of flue gas recirculation on NO_x emissions was studied in a boiler using recirculation for steam temperature control. However, this type of recirculation did not involve the injection of flue gas into the active flame zone. Consequently, results were inconclusive and this type of recirculation was felt to be relatively ineffective. Unpublished information* obtained in a similar test on a gas fired boiler, however, indicates a reduction of 20% in NO_x emissions with 20% flue gas recirculation. How much greater the reductions in NO_x might be with flue gases recirculated directly into the active flame zone of power plant furnaces is not known.

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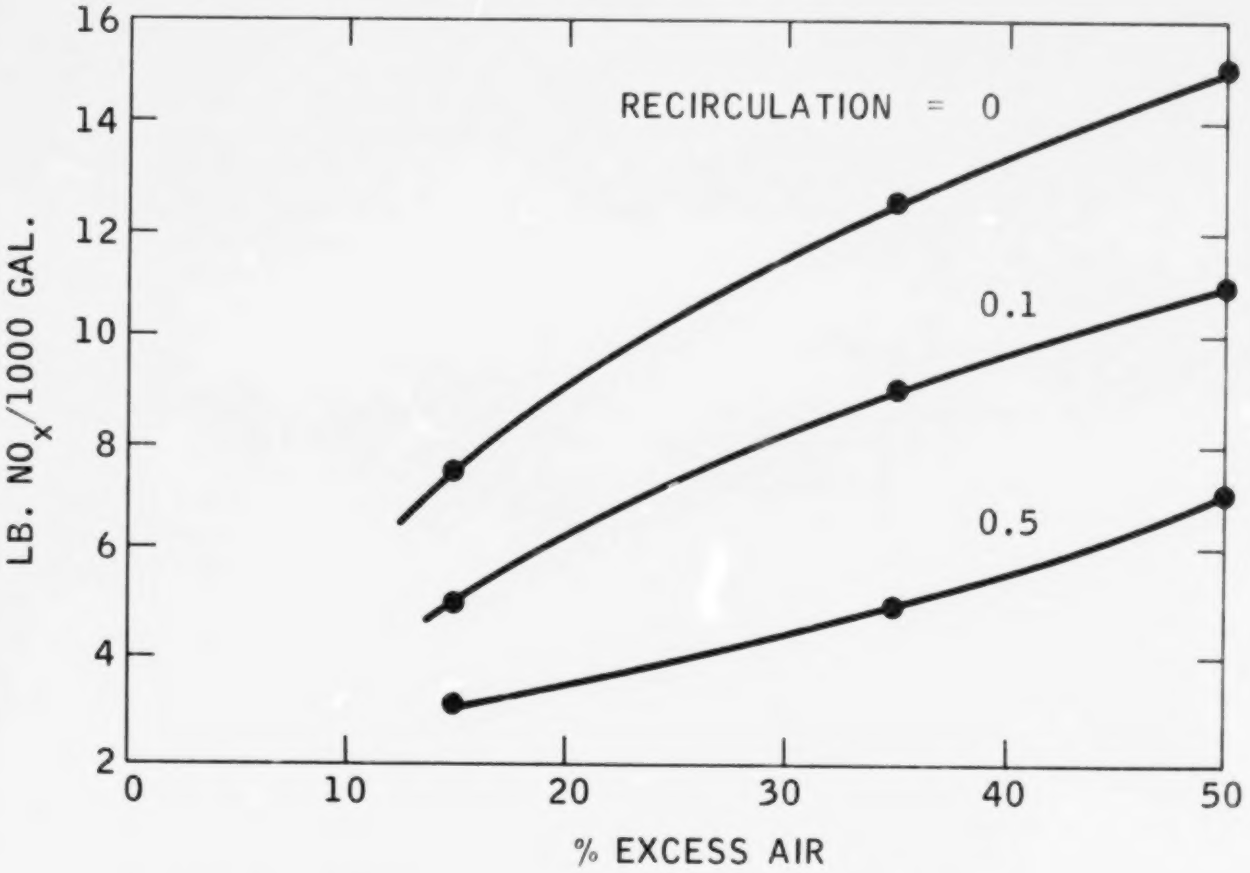
* Private communication, electric utility company.

As indicated above, the objectives of flue gas recirculation for steam temperature control in a public utility boiler may be at odds with the objectives of recirculation for control of NO_x emissions. Since NO_x production would be highest at maximum load on the boiler, it would be desirable to recirculate the largest quantity of flue gas at that load, to achieve the greatest NO_x reduction. Many recirculation systems for steam temperature control, however, recirculate little or no gas at full load and increase the quantity recirculated as load falls off in order to maintain constant steam temperature. In addition, injecting the recirculated gas through the burners would have the greatest effect on flame temperature (and NO_x) and the effect on furnace absorption may be greater or less than desired for steam temperature control. While these effects are not necessarily incompatible, they may pose conflicting problems if recirculation for NO_x control were superimposed on a boiler with an existing recirculation steam temperature control system. Even on boilers not so equipped, applications of recirculation for NO_x control will affect the ability of existing controls to maintain steam temperature. In many of these cases, however, attemperators (desuperheaters) or tilting burner types of superheat controls may possibly compensate for these effects, perhaps at the expense of a shortening in load range at constant superheat temperature. In any event, recirculation for NO_x control, especially in large utility type boilers, may present operating problems not anticipated in the original design. Further intensive study to determine the extent of these potential problems is warranted.

Exhaust gas recycling has also been found to be effective in controlling NO_x in automotive exhaust. Investigators have shown (4-49, 4-50) that 80 to 85% reduction in NO_x can be achieved in the internal combustion engine, albeit at the expense of operability. Similarly, Esso studies of recirculation in laboratory tests of an oil fired domestic heating furnace (4-45) have shown potential reductions of 60% when recycling 50% of the flue gas at 15% excess air, as shown in Figure 4-20 (4-45).

Figure 4-20

COMBINED EFFECT OF RECIRCULATION AND EXCESS AIR ON NO_x EMISSIONS*



* After Ref. (4-45).

Gas recirculation has also been employed in low temperature heating furnaces in industrial applications to achieve greater, and more uniform heat transfer into the product. Vertical shaft lime kilns often employ recirculation to control calcining temperatures more effectively. The effect on NO_x emissions in the later cases, however, is not known.

The mechanism for the reduction of NO_x emissions via flue gas recirculation has been attributed to the effect of decreasing flame temperature,dilution of the available oxygen in the flame zone (4-45), and to decreased residence time due to higher mass flow rate of gases. For gas fired appliances, it has been concluded by investigators at the Bureau of Mines that this reduction in NO_x is due mainly to the lowering of the flame temperature and not to reactant dilution (4-11). If true, the possibility of accomplishing the same end by other thermal means suggests the possibility of other solutions to the NO_x problem.

Gas recirculation, regardless of its action in reducing NO_x, offers considerable potential for application to many existing installations, with the possible exception of those dependent on high flame temperature, i.e., melting furnaces. The extent of applicability of this type of combustion modification must still be investigated. The quantity of recirculated gas necessary to achieve the desired effect in different installations is important and can influence the feasibility of the applications. For instance, recirculating large quantities of gas in utility boilers may raise physical limitation problems in handling large quantities of gas, in addition to increased investment and operating costs.

4.4.1.4 Steam or Water Injection

Flame temperature, as discussed above, is one of the important parameters affecting the production of NO_x. There are a number of possibilities available to decrease flame temperature via thermal means. For instance, steam or water injection in quantities sufficient to lower flame temperature to the required extent may offer a simple control solution. Water injection may be preferred in many cases, due not only to its availability and lower cost, but also to its potentially greater thermal effect. In gas or coal fired boilers equipped for standby oil firing with steam atomization, the atomizer offers a simple means for injection. Other installations will require special rigging, and a systematic study would be necessary to determine the degree of atomization and mixing required with the flame, the optimum point of injection, and the quantities of water or steam necessary to achieve the desired effect. The use of these techniques for NO_x control may entail some undesirable operating conditions, such as decreased efficiency, higher corrosion rates, etc., and these must also be evaluated.

As a practical assumption, as discussed in later sections, water injection for NO_x control is regarded as being unfeasible economically if injected in quantities sufficient to cause losses in efficiency greater than 1 percent. At this injection rate, it was further estimated that a 10% reduction in NO_x emissions would result. Based on this concept water injection would only be used to "trim" peak NO_x emissions.

Water injection was found to be very effective in suppressing NO_x emissions from an internal combustion engine (4-51). NO_x emissions were decreased 90% by injecting water in a 1:1 weight ratio with the fuel. Engine power increased and a slight increase in specific fuel consumption was obtained. Substantial reductions in NO_x were also obtained with moderate rates of injection lending considerable support to this technique as a method of control.

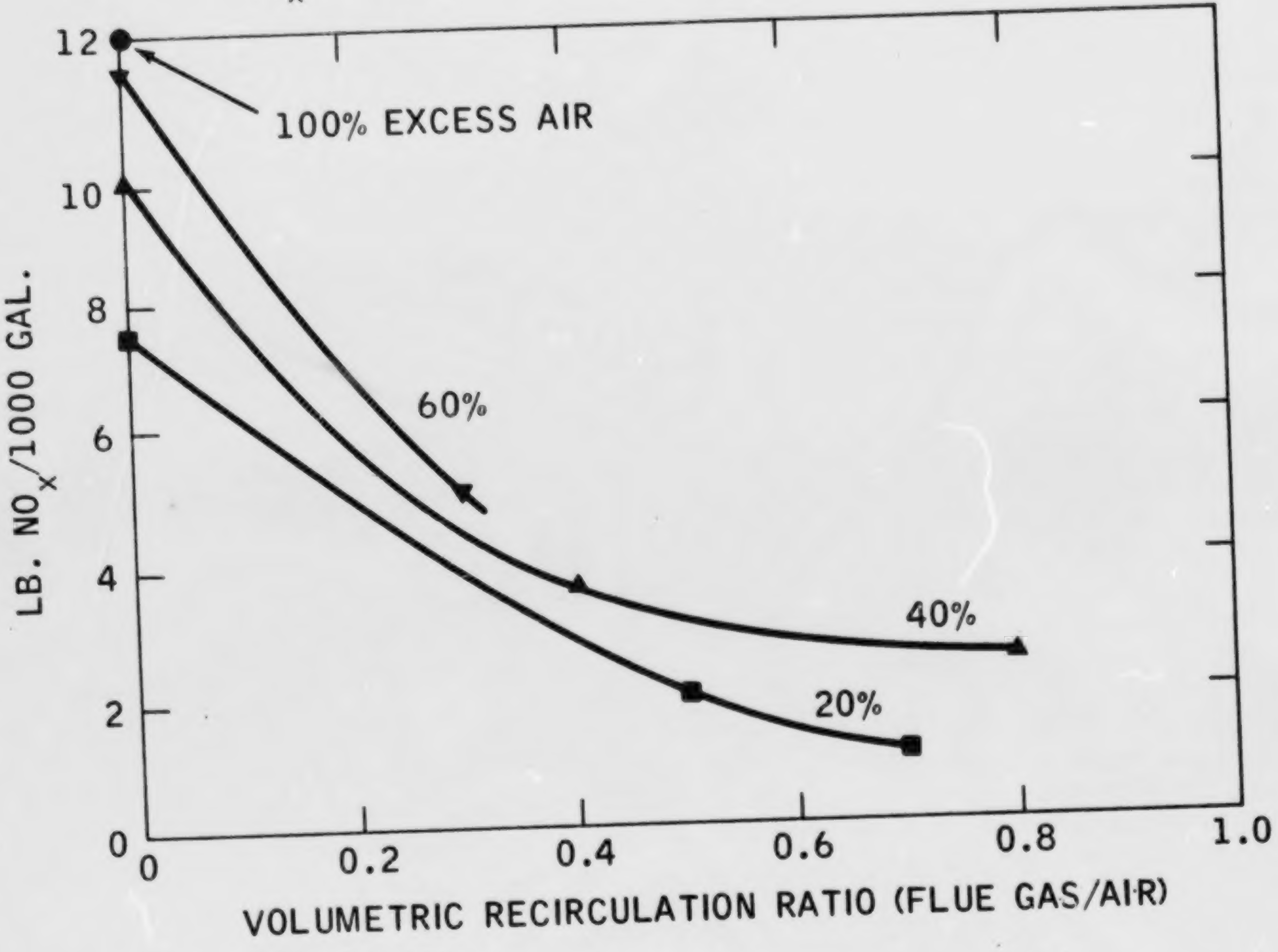
4.4.1.5 Combinations of Combustion Modification Techniques

Although the combustion modification techniques discussed above may be sufficient in themselves to achieve desired NO_x reductions, their optimum utilization would be in combinations. In fact, there is evidence of a synergistic effect in actual reported results, which is in excess of the addition of separate potential effects. For example, a reduction in NO_x emissions of 90% was achieved in a large gas fired utility boiler on the West Coast using a combination of low excess air and a modified form of two-stage combustion. Considering the potential additive effects of each technique separately would lead to the conclusion that maximum reductions of perhaps 70-80% would be realized. As mentioned previously, many utility boilers in Los Angeles County use two-stage combustion. Many of these units also employ low excess air combustion in combination with the two-stage firing techniques to achieve further favorable emission reductions. Further optimization in this sector is a distinct possibility.

The effect of flue gas recirculation for maximum NO_x suppression, as discussed above has not yet been explored nor has the potential of a combination of low excess air and recirculation been investigated in a commercial installation. Laboratory tests of an oil fired domestic heating furnace (4-45), however, have shown some very exciting possibilities. Figures 4-20 and 4-21 based on reference (4-45) indicate that reductions in emissions up to 80% can be achieved by the combination of reducing excess air from 50 to 20%, and recirculating 50% by volume of the flue gas. In addition to the reduction in NO_x, a further advantage of combining low excess air combustion with flue gas recirculation is that smokeless combustion could be achieved at a lower level of excess air.

Figure 4-21

EFFECT OF RECIRCULATION ON
NO_x EMISSIONS FROM HEATING OIL COMBUSTION*



* After Ref. (4-45).

As far as is known, the potential combination of low excess air, two-stage combustion and flue gas recirculation has not been investigated. These techniques are likely to reinforce each other, especially in gas and oil fired equipment, but some difficulties may be encountered with coal firing. In pulverized coal installations unburned combustible losses may be aggravated, and flame ignition and stability factors may be encountered. The latter effect may also manifest itself even with gas and oil firing.

Water or steam injection, as discussed, would be used primarily to "trim" peak NO_x concentrations. This technique under this concept could be used with all the other combustion modification techniques where the achievement of an incremental reduction in NO_x emission is considered essential. The costs associated with this technique, and the relatively limited effectiveness anticipated dictate its use almost exclusively in combinations with other methods of control. Future research should establish the limitations of its applications, and the effectiveness of the technique in combined applications.

4.4.1.6 Combustion Modification Control Effectiveness

The effectiveness of the different combustion modification control techniques in suppressing NO_x emissions is very difficult to predict. The potential reductions reported above appear reasonable and undoubtedly may be achieved in many installations. However, it should not be expected that equal results will be achieved in every application. Just as uncontrolled emissions vary in "sister" installations, they should also be expected to vary from one application to another. In any one installation, results will depend on the fuel fired, the firing rate, the size of the unit, the type of operation, etc. and, most important, the specific design of the equipment. Although there is justification for optimism, the effectiveness of a specific control technique or techniques for various applications remains to be demonstrated.

Since these estimates are based on limited data, they must be verified by systematic field trials. In many cases, application technology may have to be developed to achieve the indicated reductions. In the case of coal burning situations, the estimates of NO_x reduction are especially tentative. Considerable development work may be needed to achieve these estimates.

Table 4-5, Public Utility Boilers and 4-6, Industrial and Commercial Boilers, indicate the roughly estimated potential effectiveness of the various combustion control modification techniques used in calculations in Section 9 of this report. Estimates were based on actual data, where available. Otherwise a conservative judgment was made of potential NO_x reductions based on published data related to the installation under consideration. For instance, the effectiveness in reducing excess air on an industrial boiler which operates normally at relatively high excess air was deemed to be greater than a similar application in a utility boiler operating at much closer to stoichiometric conditions initially. Thus a 40% reduction was assumed possible for industrial boiler applications vs. 25 to 33% in utility boilers. Similarly, referring to Table 4-5, since the level of excess air obtainable with pulverized coal firing is not expected to be as low as with gas or oil, the estimate reflects only a 25% NO_x reduction with coal against 30 to 33% for oil and gas, depending on the size of the installation.

It may be noted from Table 4-6 that two-stage combustion has not been considered applicable to industrial and commercial boiler installations. Except for the very large size industrial boilers, most industrial and commercial boilers, especially of the packaged type, have relatively small combustion chambers. Although two-stage combustion in these units may be technically possible, it is felt that for most cases, modifications along these lines would not be practical because of space limitations.

TABLE 4-5

PUBLIC UTILITY BOILERS
ESTIMATED COMBUSTION MODIFICATION POTENTIAL CONTROL EFFECTIVENESS
% NO_x REDUCTION

Boiler Size	LEA(1)	Two-Stage	LEA + Two-Stage	FGR(2)	LEA + FGR	Water Injection
1000 MW						
Gas	33	50	90	33	80	10
Oil	33	40	73	33	70	10
Coal	25	35	60	33	55	10
750 MW						
Gas	33	50	85	33	80	10
Oil	33	40	73	33	70	10
Coal	25	35	60	33	55	10
500 MW						
Gas	33	50	70	33	70	10
Oil	33	40	65	33	65	10
Coal	25	35	55	33	55	10
250 MW						
Gas	33	45	60	30	60	10
Oil	30	35	55	30	55	10
Coal	25	30	50	30	50	10
120 MW						
Gas	33	40	53	30	53	10
Oil	30	30	45	30	45	10
Coal	25	25	40	30	40	10

(1) LEA: Low excess air firing.

(2) FGR: Flue gas recirculation for NO_x control.

TABLE 4-6

INDUSTRIAL AND COMMERCIAL BOILERS
ESTIMATED COMBUSTION MODIFICATION POTENTIAL CONTROL EFFECTIVENESS
% NO_x REDUCTION

Boiler Type and Size	LEA(1)	FGR(2)	LEA + FGR	Water Injection
Watertube Boilers				
Lb. Steam/Hour				
27,700				
Gas	40	35	75	10
Oil	40	35	75	10
144,500				
Gas	40	35	75	10
Oil	40	35	75	10
36,100				
Coal	40	35	75	10
187,500				
Coal	40	35	75	10
Firetube Boilers				
Boiler Horsepower				
107				
Gas	40	35	75	10
Oil	40	35	75	10

(1) LEA: Low excess air firing.

(2) FGR: Flue gas recirculation for NO_x control.

For refinery process furnaces, flue gas recirculation has the greatest potential of the NO_x control methods. Applications of this technique could be readily incorporated in new furnaces and conversions could be considered for existing installations. A reduction in NO_x emissions of 33 1/3% has been considered possible for the average installation and calculations in later sections of this report are based on this decrease. Other methods of NO_x control are less likely for refinery furnace as several factors mitigate against two-stage combustion and very low excess air rates in furnaces of this type. Excellent combustion conditions are required to prevent hot spots and coking inside furnace tubes as well as corrosion of tube hangers. Two-stage combustion produces long smoky flames which impinge on furnace tubes. Most furnaces are of the natural draft design, and the air rate is controlled by damper setting. Furthermore, many furnaces burn by-product gas or liquid fuels of fluctuating composition and heat content. Thus, inadequate control of air rate and fluctuating fuel quality limit the reduction in excess air.

4.4.1.7 Combustion with Oxygen or Enriched Air

Economics have been achieved in the steel and metal industries in certain processes by substituting oxygen for air. As a result, the cost of oxygen has decreased to a point where its use in some combustion processes may become feasible. Impure oxygen or enriched air could effect even further economics. However, as discussed in Section 4.3.2.3, the higher flame temperatures reached in firing with oxygen, even with only small amounts of nitrogen present, are likely to negate any potential NO_x control. Furthermore, as discussed before, the chemically bound nitrogen in coal and fuel oil would be converted into significant amounts of NO_x.

4.4.2 Modification of Design Features

Certain specific combustion equipment has been observed to produce higher NO_x emissions than others of equal size. Comparison reveals fundamental differences in configuration and design principles. Some of these differences evolved as dictated by economics, others resulted in the scale-up of size, and still others by the development of specific processes, designs, burners, combustion systems, etc. by certain manufacturers. Although economics may prevent alterations in design features aimed at lower NO_x emissions for existing installations, there is no reason why optimized economic designs should not be adopted for new installations. The most important design features known to have an effect on NO_x emissions are discussed below.

4.4.2.1 Burner Configuration, Location and Spacing

The specific design and configuration of a burner has an important bearing on the amount of NO_x formed. Certain design types have been found to give greater emissions than others. For example, it appears that the spud type gas burner gives a higher emission rate than the radial spud type which, in turn, produces more NO_x than the ring type. Similarly, the spray angle in oil atomizers can affect NO_x; narrower spray angles producing poorer atomization, have been reported to provide lower NO_x emissions (4-48) as opposed to the results of Barnhart and Diehl (4-46).

Some burners, such as the cyclone and vortex types, operate under highly turbulent, high intensity conditions. In field tests of conventional utility burners (4-48), adjustments made on burners to decrease turbulence to a minimum, resulted in reducing NO_x emissions by 40%, but also, in unsatisfactory flame conditions. Throttling the burner registers to increase windbox pressure and turbulence increased NO_x emissions by more than 15%. Delayed mixing of the fuel and air, especially if accompanied by operating the burners at less than the normal amounts of combustion air, tends toward lower NO_x production (4-46). In general, long "lazy" flames in contrast with the short, intense flames usually considered desirable for combustion seem to favor lower NO_x emissions.

Although data are scarce regarding the effect of burner spacing and location on NO_x, potentially these are important variables. The interaction between closely spaced burners, especially in the center of a multiple burner installation, could be expected to increase flame temperature at these locations. The tighter the spacing and the lower the ability to radiate to cooling surfaces, the greater the tendency toward increased NO_x emissions. This effect is illustrated by the higher NO_x emissions from larger boilers with greater multiples of burners and tighter spacing, as discussed in Section 4.2. In the course of the California investigations in the early 1960's, as discussed in Report 3 of reference 4-52, tests were conducted on large boiler units where the number and spacing of burners in use were varied. It was reported that when the burners in operation were closely grouped or when more burners were in use, more NO_x was produced than when the same amount of fuel was burned, using fewer burners with wider spacing. These results were attributed to the relative amount of cold waterwall surface "seen" by each burner. Less NO_x is formed when more cooling surface is available to absorb radiant heat from each individual burner flame.

4.4.2.2 Tangential Firing

Since the NO_x formation reaction is strongly dependent on temperature, any combustion method resulting in lower flame temperature should lead to lower NO_x emissions. One approach is to use the tangential firing concept (4-50), which uses the furnace itself as the burner and inherently produces lower peak flame temperatures. Tangential firing has been demonstrated as a very useful design concept, representing a change from other types of burner location and spacing. Burners in a tangentially fired boiler are located in the corners, firing on a tangent to a circle at the center of the furnace. As a result, individual burner flames have very little opportunity to interact with one another and the flames radiate widely to the surrounding cooling surfaces. The effect is a parallel to the results obtained in California as noted in the section directly above regarding spacing of burners. Tangential firing can produce reductions in NO_x emissions upwards to 60% compared with front or opposed wall furnaces (4-50). This significant effect requires further evaluation for potential NO_x control in other types of combustion processes. Based on the available information, tangential firing for new furnace installations must be regarded as holding equal promise to that of other combustion modification methods utilizing similar principles. Specifically, optimized two-stage combustion with front or opposed-wall fired furnaces is estimated to be at a standoff from the point of view of potential NO_x control with optimized tangential firing. Future research and test programs on NO_x emission control should consider tangential firing in combination with other control methods.

4.4.2.3. Fluidized Bed Combustion

Combustion of fossil fuels in fluidized beds may prove a useful way of controlling NO_x emissions. A fluidized bed boiler has several potential advantages compared to a conventional boiler. It can, for example, burn a wider range of solid and liquid fuels than can be handled in conventional steam raising equipment. Coal need only be crushed rather than pulverized, and the more uniform and lower fluidized bed combustion temperature (typically 1500 to 1800°F)would limit boiler tube corrosion and formation of fireside ash deposits. Another advantage of fluidized bed combustion is that it provides a contactor that can be used for SO_2 control. The Pope Evans and Robbins Co., and the Argonne National Laboratory in the United States, and BCURA Industrial Laboratories and Esso Ltd. in England, have all shown that the use of limestone and dolomites in the fluidized bed combustor can control SO_2 emissions (4-53).

Fluidized bed boiler costs may be lower because of the high heat release and transfer rates possible in this system. One estimate has been made that a four-fold reduction in boiler tube costs could be achieved based on the 50 to 100 $BTU/ft^2/hr/°F$ heat transfer coefficients that have been observed in fluidized bed boilers. According to this same estimate, this and other improvements made possible by the fluidized system would reduce operating costs by about 10% for a 500 MW station. Studies made by BCURA Industrial Laboratories (4-53) indicate a 50 to 65% reduction in boiler volume by operating it as a fluidized bed.

The potential of fluidized bed combustion for NO_x control results from the fact that the average and peak combustion temperatures are relatively low compared to conventional combustion. Because of this, both the kinetics and thermodynamics are unfavorable for reaction between molecular oxygen and nitrogen. In spite of this favorable outlook, data obtained by Pope, Evans and Robbins and by the Argonne National Laboratory have indicated emissions comparable to conventional combustion (4-53). For example, Pope, Evans and Robbins measured about 0.3 lbs. $NO_x/10^6$ BTU fired in their coal burning pilot unit, which is about the same as the emissions measured from stoker-fired units of similar capacity.

Data obtained by Argonne National Laboratories show the nitrogen oxides in fluidized bed combustion to arise from oxidation of organically bound nitrogen in the fuel. (4-17(Thus, the substitution of an argon-oxygen mixture for air in one of their fluidized bed combustion experiments on coal produced no decrease in NO emissions.

Controlling nitrogen oxide emissions arising from combustion of the more reactive fuel nitrogen presents a different problem from control of NO produced by N_2-O_2 reaction. Those combustion control methods aimed at reducing average and peak flame temperatures will be of limited or no effect. The possibility exists, however, of reducing NO emission in fluidized bed combustion by operating the bed as part of a two stage combustion system or by incorporating additives in the bed that are capable of promoting the decomposition of NO. As indicated in Section 5.2., alkaline and alkaline earth oxides appear to catalyze the decomposition of NO. These are the same type additives being considered for SO_2 emission control. Argonne National Laboratory has in fact shown, that injection of finely sized limestone into a fluidized bed of combusting coal to capture SO_2 reduces NO emission by 25 to 30%.

Esso Ltd. has proposed operating fluidized combustors with substoichiometric air (4-53). Combustion of the gases from the bed can then be completed in a second stage above the bed. It can be speculated that emissions from such combustion would be even lower than those from two-stage combustion carried out in conventional furnaces. Experimental work is needed to confirm this concept.

4.5 CONTROL OF NO_x EMISSIONS FROM STATIONARY INTERNAL COMBUSTION ENGINES

The control of NO_x emissions by modification of engine design, operating conditions, fuel type, and water and recycle gas injection and exhaust gas treatment will be discussed. The sections immediately following are specifically applicable to reciprocating piston engines. Turbine engine modifications are then discussed.

4.5.1 Reciprocating Engines

Combustion Chamber Design - The beneficial effect of the precombustion chamber (see Table 3-9) suggests that combustion chamber design and modification may have a large effect on NO_x emissions. The precombustion chamber provides a type of two-stage combustion with the first stage under extremely rich conditions and the second stage very lean. It can be readily applied to fuel oil-fired piston engines. It does not seem that it could be easily adapted to the gas-fired type. It might add slightly to the first cost of the engine and there may be an adverse effect on thermal efficiency if the engine is operated under conditions differing from optimum design. Examples of precombustion chamber engine designs are the Caterpillar engine, the M.W.M. (Motoren-Werke Mannheim), the Mercedes-Benz OM-621, and the larger Daimler-Benz diesels.

Other combustion chamber modifications that may influence NO_x emissions and require investigation include the use of turbulence chambers (as used in engines manufactured by International Harvester, Waukesha, John Deere, Deutz) and "energy cells" (in Minneapolis-Moline engines). The latter provides controlled combustion to prevent high peak pressures and rough operation.

Fuel Type - There are some indications that increasing fuel API gravity (i.e., decreasing specific gravity) is accompanied by a decrease in NO_x emissions in a diesel engine. This is shown in Table 4-7. There is about a 25% decrease in NO_x production when the API gravity of the fuel is increased from 30.9 to 42.8° API. The trend is also supported by the low emissions obtained with natural gas. There are, of course, accompanying changes in boiling range, viscosity, and cetane number, and the effect of the latter is probably significant also. It is not clear which is the controlling variable, although the mid-boiling point (or viscosity) gives the most consistent trend. It thus appears that it may be possible to modify NO_x emissions by tailoring fuel properties. However, it will be appreciated that the use of special fuels will add to fuel costs because of problems associated with availability, refining, and marketing.

Exhaust Recycle - This has been shown to be an effective means of controlling NO_x emissions in gasoline engines, furnaces, as discussed in Section 4.4. It may also reduce NO_x from diesel engines as the (fresh) air to fuel ratio is held constant, but testing will be required to confirm this. It will probably mean a decrease in the maximum power capability of the engine and will require a modest increase in cost due to the need for additional piping and a control mechanism.

Optimum Air/Fuel Ratio - Most stationary diesel engines' maximum power setting is limited by smoking (at say 20/1 air/fuel ratio). It is possible, therefore, to vary air/fuel ratio only by reducing the amount of fuel injected resulting in a proportional increase in the air/fuel ratio (and a corresponding decrease in power). The indications are (4-54)) that as fuel rate is reduced, NO_x emissions in lbs./hr are a linear function of power. This means that the rate of NO_x formation/lb. of fuel (or million BTU) is constant (over the range in which specific fuel consumption is constant), and no benefit results from the overall leaner (high air/fuel) operation.

Gas engines, on the other hand, are usually set at an air/fuel ratio giving maximum economy of operation (about 2.5% excess oxygen equivalent to about 19/1 air/fuel ratio). As shown in Table 4-8, this is very close to the conditions at which maximum NO_x production is obtained. Table 4-8 also indicates that NO_x production can be reduced by moving to either richer or leaner operation. Using richer mixtures runs the risk of increasing the emissions of unburned hydrocarbons and carbon monoxide. This hazard can be avoided by using higher air/fuel ratios. For example, with methane it is possible to operate with only 70% of the stoichiometric amount of fuel without running into misfiring of the engine. At this point, NO_x emissions are reduced to about 30% of their maximum value. The penalty for this type of operation is a loss of power (e.g. 30% at 70% stoichiometric fuel) which is equivalent to a 30% increase in the first cost of an engine.

The reason why adjustment of air/fuel ratio controls NO_x emissions in gas engines, and not in injected diesels is because the gas engine operates with a premixed, homogeneous air/fuel mixture. Thus, flame temperatures are reduced at high air to fuel ratio. This is not the case with the heterogeneous air-fuel mixture present in a diesel engine in which liquid fuel is sprayed into the air in the combustion chamber and combustion takes place in fuel-rich places.

Water Injection - Water injection appears to have the greatest promise of potential methods of controlling emissions from spark fired gas engines. Tests on laboratory engines indicate that water injection into the intake manifold reduces NO_x with no decrease in maximum power or fuel economy (4-51). At 93% of theoretical fuel, NO_x was reduced from 3000 ppm with no water injection to about 700 ppm at a water injection rate of 1.25 lbs/lb of fuel. Water injection was even more effective for rich mixtures.

TABLE 4-7

EFFECT OF FUEL TYPE ON EMISSIONS OF NO_x FROM A STATIONARY DIESEL ENGINE[a]

	Fuel Characteristics						NO_x Emissions	
				B.P. °F				
Reference	° API	% Arom. (FIA Anal.)	Est. Net Heat. Value BTU/lb.	50% Dist.	Final B.P.	Vis. SUS @ 100°F	lbs.NO_x/lb. fuel	lbs./10^6 BTU
4	42.8	12	18,570	428	514	33.0	0.23	12.4
4	32.7	28	18,300	500	609	34.3	0.23	12.6
4	32.4	--	18,290	519	661	36.1	0.3	16.4
4	30.9	26	18,220	538	656	38.0	0.3	16.5
8	Methane	0	21,500	-259	---	---	0.056[b]	2.6[b]

(a) Precombustion Chamber, turbo charged, rated speed, about 25/1 Air/Fuel ratio.

(b) Actual data doubled to correct for turbo charging; data at full throttle, 72% Max. IMEP and 72% stoichiometric fuel, i.e., A/F = 24.

TABLE 4-8

EFFECT OF AIR/FUEL RATIO ON NO_x PRODUCTION IN SPARK IGNITED STATIONARY GAS ENGINE (4-54)

(Full Throttle, Max. Power Spark, 1,000 RPM, Compression Ratio - 8/1, Fuel - Methane)

% Stoichiometric Fuel	$^{\text{lbs. Air}}/_{\text{lb. Fuel}}$	Power % Max. IMEP	NO_x Production lbs. NO_x/lb. Fuel	 lbs. $NO_x/10^6$ BTU
100	17.1	88.9	0.0038	0.18
95	18	---	0.0065	0.30
92	18.6	---	0.0095	0.44
87	19.7	80	0.0069	0.32
84	20.4	78	0.0055	0.26
70	24.4	71	0.0028	0.13
65	26.3	misfire	--	

Modified Fuel Injection Timing - It is possible to vary the pressure and temperature conditions in an injected diesel engine by changing the timing of fuel injection. This might include changing the point in the cycle at which fuel injection is started and/or the rate of fuel addition. Two-stage fuel injection is also a possibility. The effect of these variables on NO_x production requires clarification. They will also probably affect power output and/or thermal efficiency.

Variable Compression Ratio - Variable compression ratio-compression ignition engines have been developed for military applications (4-55). The compression ratio is changed by hydraulically raising or lowering the height of the top of the piston. The system tends to maintain a preset peak combustion pressure in the combustion chamber. Presumably, this would avoid the excessively severe cycles which occur frequently (4-56) in the conventional diesel engine and which might account for a disproportionate part of the NO_x emissions. The NO_x emission characteristics of the variable compression engine are thus of considerable interest.

Variable-compression pistons are probably more expensive than conventional pistons and may require somewhat more maintenance.

Treating Exhaust - NO_x can, of course, be controlled by removal from the exhaust gases. The various possibilities would be analogous to the methods developed for stack gas treatment, discussed in Section 5. Complicating factors peculiar to the diesel engine may be the larger amounts of air used in the diesel cycle (30% or more above stoichiometric requirements) and a relatively low exhaust temperature. Adding control equipment to an engine for exhaust treatment will obviously increase first costs and operating costs.

Rich Engine Plus Exhaust Reactor - By operating a spark ignition engine in the rich region, NO_x emissions are reduced, but hydrocarbon and CO emission are increased. All three pollutants can be controlled by operating the engine rich, and oxidizing the hydrocarbons and CO leaving the engine by injecting air into the exhaust in a thermal reactor. Specific fuel consumption rises, and initial costs are increased.

4.5.2 Turbines

Long range, NO_x, can be cut by using gas turbine drivers in new installations and replacing wornout units with gas turbines. Gas turbines consume about 11,000BTU/HP-Hr, compared to about 6,600 for piston engines (4-57). However, the cost of modified aircraft turbines are about $110/HP vs about $300/HP for reciprocating engines. In the popeline industry, the current trend is toward turbines which are better adapted to automation.

Combustion Chamber Design - Exhaust recirculation has been discussed in Section 4.4 as capable of making marked reductions in NO_x emissions in an oil-fired domestic heater. It would seem possible that an analogous type of recirculation can be developed within the combustor of a gas turbine engine with similar beneficial effects on NO_x emissions.

Two (or more) stage combustion is also an effective general method for holding down NO_x formation. In this type of operation, initial partial combustion is carried out in a rich primary zone after which combustion is completed by the addition of more air. The beneficial effect is probably due to keeping combustion temperatures down and restricting the availability of oxygen during the critical combustion phases.

Thus, it appears that studies of combustor design directed toward promoting internal exhaust recirculation and controlling oxygen availability would be fruitful approaches to reducing NO_x formation in turbine engines. While such studies have not yet been reported, it is believed that improved combustors could probably be developed without any major increase in cost. The effect of design changes on important, turbine performance criteria would need to be studied to determine what penalties would be involved by this approach.

Effect of Fuel Composition - It is well known that the radiative emissivity of a flame in a gas turbine engine increase as the hydrogen content of the fuel is decreased. This suggests that the temperature of the flame from a fuel with low hydrogen content may be lower (because of increased radiation to the combustor walls) than that from a fuel containing more hydrogen. Thus, NO_x emissions in turbine engines may vary with fuel characteristics. Data are required. It will be appreciated, of course, that the use of special fuels usually results in an increase in fuel cost.

Fuel Additives - The potentialities and problems of this approach to reducing NO_x emissions from the gas turbine engine are essentially the same as was discussed above in connection with the diesel engine.

Treating Exhaust - The considerations here are essentially the same as with the diesel engine with the added complication that the turbine utilizes about twice as much air.

Reduce Turbine Inlet Temperature - Gas turbine efficiency depends directly on the differences between the inlet and outlet temperatures, so any change which lowers the inlet temperature requires a larger turbine for a given power output.

It is possible that NO_x emissions can be lowered by reducing turbine inlet temperatures. For example, observations demonstrate that the NO_x level is determined by the extent of the formation reaction at the time of thermal quenching (4-58). It appears that at low turbine inlet temperatures, this quenching occurs earlier in the formation reaction than at higher turbine inlet temperatures (see Table 4-9). The drop in NO_x formation at the higher air/fuel ratios (i.e., lower turbine inlet temperature) is probably because of the larger quench air ratio (higher excess air/fuel ratio).

This effect requires clarification. However, the penalities for such a step are reflected in installation and operating costs. It is estimated that a 100°F decrease in turbine inlet temperature will decrease power by 10% and will increase fuel consumption by about 5%.

TABLE 4-9

EFFECT OF AIR/FUEL RATIO[(a)] ON NO_x FORMATION IN AN EXPERIMENTAL COMBUSTOR RIG (13)

A/F Ratio lb. air/ lb. fuel	Relative Temperature at Exit of Combustor, °F	NO_x Concentration PPM As Measured	NO_x Concentration PPM Corrected to 15/1 A/F	NO_x Lbs/Lb Fuel (Calc.)
53	T	34	120	0.0017
73	T minus 370	10	50	0.0007

(a) Directly related to temperature of the gases at combustor exit.

4.6. OTHER COMBUSTION SOURCES

A number of combustion sources involve unusual furnace configurations which pose control problems differing from conventional sources such as utility and package boilers. Controls for these sources are discussed below.

4.6.1. Metallurgical Furnaces

Emission controls in the steel industry and related processing have been concerned with fumes, smoke, and dust or particulates. The gases usually considered obnoxious have been SO_2, CO, and odors. The presence of oxides of nitrogen has been obscured by the heavy emission of particulates and the resulting lack of physical evidence of their presence. The NO_x emissions observed can be traced largely to the combustion of fuel oils and gas, and in part to the burning of carbon monoxide which is a product of the processing operations.

Equipment and processing changes intended for the abatement of air pollution must consider the effect on NO_x emission, e.g., higher temperatures increase NO_x production. On the other hand the major shift now in progress from open hearth to BOF in steel production promises a substantial reduction in NO_x emission. The only NO_x produced in the BOF process is believed to result from the burning of the carbon monoxide produced in the operation. This may be controlled by proper hooding and gas collection which may be a minor source of NO_x when used as fuel.

Regenerative type furnaces will be used in one capacity or another for some time, and these may be subject to at least partial control of NO_x in combustion processes as outlined in Section 4.4. In brief these deal with:

1. Avoiding excess air which limits the presence of one of the reactants in NO_x formation regardless of the resultant increase in flame temperature.

2. Avoiding high peak tempeature, to the extent that the operation will permit.

3. Avoiding turbulence and condensed flames in which isolated high temperature zones can exist.

4. Consideration of burner type and placement.

5. Staged combustion in which less than stoichiometric air is initially provided to the flame, and air to complete combustion is supplied at a later stage in the combustion.

6. Recirculation of combustion products or addition of other generally inert gases such as steam.

Removal of NO_x from the products of combustion by scrubbing or adsorption have not as yet reached a stage of development which seems practical for metallurgical applications.

The use of electrical heat is growing rapidly, and this transfers the NO_x emissions to the utility plant where it is expected to be easier to control. Projections to 1980 indicate that raw steel production will reach 180 MM tons of which 45 MM (up from 13 MM tons in 1967) will be produced in electric furnaces (4-59).

Electric induction heating will reduce NO_x emission at the furnace to the extent that fuel combustion is displaced. On the other hand, electric arc heating does produce NO_x. However, no quantitative data appear to be available.

The projected use of the plasma arc furnace, (4-60) may also be a substantial NO_x producer, and these processes may require some form of inert blanketing if they are to avoid problems with air pollution.

4.6.2. Cement, Lime and Ceramic Kilns

The literature shows no references to commercial installations of equipment for removing NOx from kiln waste gas or of modifications to kiln operations to reduce NO_x production. Water scrubbing is sometimes used for particulate removal in waste gas from lime kilns. In this operation, the gas contacts a slurry of calcium hydroxide, which should remove a 50/50 mixture of NO and NO_2 and reduce NO_x up to 20%.* Flue gas recirculation, which is used to control temperature in some lime kilns (4-20), should reduce NO_x emissions by lowering flame temperature.

It is recognized that combustion gas in lime kilns contacts calcium oxide and calcium carbonate as it passes through the kiln, and some NO_x probably reacts to form calcium nitrate and calcium nitrate salts. The nitrites and nitrates would subsequently decompose in the high-temperature zone of the kiln, releasing any NO_x which had reacted. Thus, it is unlikely that contact between the combustion gas and lime or limestone in the kiln results in an overall reduction in NO_x emissions.

Several of the possible means of reducing NO_x emissions in kiln operation are the same as in the high-temperature combustion discussed in detail in Section 4.4. These include:

1. Conversion to oil and preferably to gas firing. However, advantage should be taken of the economic aspects of an intermittent gas supply by retaining an alternate firing means.
2. Keep excess air to a minimum.
3. Automatic control of firing variables.
4. Modification of firing design such as burner location.
5. Lower peak flame temperature to the extent allowed by the process.

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* See discussion in Section 5.5.1.

Electrical heating eliminates all the pollutants associated with combustion sources, but its use in kiln operations is very limited. Other control means particularly applicable to kiln operation are limited to choice of kiln type. As shown in Table 3-12, some NO_x reduction in limestone calcining is obtained by using a vertical kiln vs. the rotary, but this is based only on the lesser fuel consumption. The higher thermal efficiency, lower capital and operating cost and increased capacity of recent designed vertical kilns may result in a long-term trend away from rotary kilns.

Scrubbing as a means of NO_x reduction is not as yet feasible for combustion gases. Section 5 describes the progress that has been made in this area.

4.6.3. Glass Manufacture

Controls for NO_x emissions have not been developed for the glass industry. Combustion modifications for reducing flame temperatures do not appear applicable, since high flame temperatures are required to heat the charge to the 2600-2850°F temperatures required in glass melting. Low excess air operation might lower NO_x levels while maintaining or increasing temperature; it would require improved controls. Automatic controls, and changes in burner positioning are potential methods of reducing NO_x.

Measures which may be specific to glass melting are:

1. Minimize hot spots within the furance. It is known that minute changes in residence time in extremely high temperature zones can considerably effect NO_x emission.

2. The end-fired tank which uses a single large burner with long path travel might cause less NO_x formation. A large, luminous flame is known to produce less NO_x than an intense restricted flame.

3. Electrical heating as a booster source is used to advantage when high temperature or increased production are desired. It is favored for colored glasses and tends to extend refractory life. An all-electric melter requires less capital investment than conventional melters (4-61). From the pollution standpoint, electric heating reduces NO_x emission to the extent, at least, that combustible fuels have been displaced. However, the economics involved are not clearly in favor of electric heating except as a "booster", since for most locations, power is a more costly source of energy than fuel, even when allowing for higher efficiency - say 75% for power compared to 15-20% for fuel (4-61). The use of power transfers NO_x emissions to the power plant.

4. Oxygen enrichment is another method for increasing the capacity of a furnace and is sometimes less costly than electrical heating (4-62). Oxygen enrichment would increase NO_x emissions, except when pure oxygen replaces all combustion air to the furnace. The complete replacement of combustion air would be very uneconomical.

Small room-scale or laboratory (4-63) operations with high-temperature flames such as frequently used in bench-type glass work operations, particularly if oxygen-enriched, are a potential high level source of NO_x. It appears that such operations plus the smaller pot-type glass furnaces can be suitably hooded and the exhaust gases adequately dispersed.

4.6.4. Incineration and Waste Disposal

Substitution of non-combustion alternative waste dispositions may be the most likely means for reducing NO_x emissions, since the methods normally used for control of other emissions from incineration such as particulate matter, organics and carbon-monoxide tend to increase emissions of NO_x. The reduction of NO_x emissions by some of these methods and by changing combustion conditions in incinerators are discussed as follows:

4.6.4.1. Waste Disposal

From the standpoint of air pollution, the most satisfactory method of waste disposal is to avoid burning. Sanitary land fills are good alternates, to the extent that land usable for this purpose is available. Approximately one acre-foot of land is required per 1000 persons per year of operation when waste production is 4.5 pounds per day per capita (4-64). In addition, cover material approximating 20% by volume of the compacted waste is required and the availability of cover material may limit the use of sanitary land fill.

Other non-combustion alternatives may have application in some localities. Composting has been considered and is being tested on a practical scale, (4-65) and hog feeding has been used for disposal of garbage. Dumping at sea has been practiced by some seacoast cities, but some of the garbage floats and returns to shore unless dumped at excessively far out distances. Such practices are now forbidden by the U.S. Government.

Incinerators which reduce NO_x by changing combustion conditions are not available except on a developmental basis. Most incinerators are not provided with means to remove the heat of combustion. Accordingly, the burning rates must often be curtailed and overfire air provided in order to protect the incinerator from heat damage. Gas temperature should exceed 1400°F in order to consume carbon particles, organics, carbon monoxide and odorous compounds. Temperatures in excess of 1800°F cause sintering of ash particles, which can cause undesirable accumulations (4-66).

Data are rather firm in showing that excess air increases NO_x emission regardless of the cooling effect it has on the gas temperature. An increase from 50 to 300% of excess air caused a 32% increase in NO_x per lb of waste burned (4-67). This same reference shows that moisture content of the waste does not appreciably effect the NO_x/lb of waste burned, but does increase it on a dry basis. Rose and coworkers (4-68) showed an average value of 1.96 lbs of NO_x/ton of waste at 50% excess air and 2.19 at 150% of excess air for an increase of 12%. Also, an increase in gas temperature from roughly 1500 to 2300°F caused the NO_x concentration to increase from 50 to 100 ppm. As expected, feed rate also increased the emission of NO_x/unit weight of waste.

Various incinerator types may use auxiliary fuel for such purposes as waste drying, start-up, supplemental heat and afterburning. Either oil or gas are used and the NO emitted is, in part, due to the auxiliary fuel. For example, (4-69) in one domestic garbage incinerator designed for low particulate and organic emissions, natural gas burned to increase heat input to 15,000 Btu/lb of waste as compared with a heating value for garbage in the order of 2500 Btu/lb. The NO emissions from burning 12.5/ft^3 gas/lb of garbage are estimated at 2.9 lb/ton of garbage which is a very substantial increase as compared with estimates of emissions without gas burning of the order of 1 lb/ton (4-15). Figures for a flue-fed incinerator (4-15) are 10 lbs NO_x/ton with an afterburner and 0.3 without. These data suggest that the NO_x emission from the incineration of refuse is substantially increased by the auxiliary firing of oil and gas fuels.

One way of reducing total NO_x emissions from incineration is to recover heat in a boiler, thus replacing combustion of some fossil fuels. This means of refuse disposal has already received considerable attention in Europe as indicated by the several references (4-70, 4-71, 4-72, 4-73, 4-74).

In 1966, two 50 thousand pound per hour steam generators were installed at the Navy Public Works Center, Norfolk, Virginia (4-75) which were designed to burn 180 tons of mixed refuse per day in each of two furnaces. The heating value of the mixed refuse is estimated at 5,000 Btu/lb with a 25% moisture content and 12.5% non-combustibles. Steam is generated from the combustion of the refuse. The waste fired is supplemental by oil firing as required. The furance walls are water-cooled and intergral with the boiler which reportedly increases steam production by 38%. This feature permits the use of low excess air which favors reduced NO_x emission.

4.6.4.2. Burning of Agricultural Wastes

As collection and incineration of these materials would tend to increase NO_x emissions, the only currently available control techniques involve avoiding combustion. In the future it may be possible to develop incineration processes which would control NO_x emissions and other emissions as well as particulates, organics, odorous compounds, and carbon monoxide or to develop equipment to burn these materials as substitutes for fossil fuels.

Other alternatives to incineration are abandonment or burying at the site, transport and disposal in remote areas, and utilitzation. Abandonment or burning at the site is practical in cases where no other harmful effects will ensue. As abandoned or buried vegetation can have harmful effects upon plant life such as by hosting harmful insects or organisms, agricultural agencies such as the U.S. Department of Agriculture or state and local agencies should be consulted before these techniques are recommended. Other harmful aspects such as odor or water pollution potential or fire hazards must also be considered. Collection and transport of these materials for disposal in areas where harmful effects are avoided is possible but not commonly practiced.

At times, it is possible to use some of these waste materials. Larger forest scraps are processed by chipping or crushing and are used as raw materials for kraft pulp mills or processes producing fiberboard, charcoal briquetts or synthetic firewood (4-76). Composting or animal feeding are other possible alternatives to burning (4-65).

4.7 SUMMARY OF HIGHLIGHTS

Combustion modification is clearly a highly attractive approach to the control of nitrogen oxide emissions. Theoretical considerations indicate that NO_x may be lowered by combining the following factors:

(1) Lowering the effective residence time of the combustion gases at the peak flame temperatures of the combustion process. This effect may be accomplished by

- lowering the peak flame temperature,
- increasing the rate of heat removal, or
- combining high heat release rates with high heat removal rates, if suitable designs can be developed.

(2) Limiting the availability of reactants. Specifically, this must consist of operating at low excess air levels, i.e., limiting the supply of oxygen. Attempts to control NO_x emissions by lowering the supply of nitrogen have been shown not to be attractive.

Our "first-generation" mathematical model is capable of predicting directional effects of changing operating and design parameters on NO_x emissions. This model will lend itself to extending its scope to provide more realistic estimates of NO formation and decomposition rates. This will require incorporating additional kinetics, heat and mass transport effects, and the inclusion of fuel oil and coal particle combustion processes. Basic laboratory studies are needed to fill the gaps in available information pertinent to the formulation of more sophisticated models, including the quantitative effect of the oxidation of chemically bound fuel nitrogen. Ultimately, a refined mathematical model should result, capable of guiding the design of low NO_x (as well as unburned fuel and carbon monoxide) emitting combustion equipment.

To date, the most widely demonstrated successful combustion modification technique for NO_x control is firing with low excess air. Data are available, on a limited basis, indicating the potential of low excess air firing varying from small domestic combustion sources to large power plants. However, no test data are available on low excess air firing with pulverized coal. A large scale R&D effort is needed for the solution of the coal-fired emission problem.

Reduction to practice of the control of the temperature-time history of combustion gases has been achieved by specific modifications for oil and gas firing. These are typified by the "two-stage" combustion technique (in combination with low excess air), and tangential firing, which seem effective in dissipating the heat of combustion, so that lower peak temperatures, and hence lower NO_x emissions result.

Flue gas recirculation (and possibly water injection for peak temperature shaving) also appear to be technically attractive for peak temperature and NO_x emission control. For stationary internal combustion engines (where large gas engines are the primary problem), laboratory data suggest the feasibility of NO_x control via water injection or flue gas recirculation.

A point of paramount importance is that combinations of combustion modification techniques are not simply additive in their effect on NO_x emissions, but that synergistic coupling of several techniques is possible. This statement is true, at least in principle, based on the very limited amount of actual measurements available.

Clearly, a systematic study of combustion modification techniques is needed, to define the scope of applicability of presently known techniques, and to take advantage of the improved understanding of factors affecting NO_x emissions, which should be obtained through basic laboratory studies combined with mathematical modeling simulations.

A special category of "combustion modification" is a new design principle, fluid bed combustion, now under development. This technique has the potential of controlling both SO_2 and NO_x emissions, and offers (among others) the advantage of very high heat transfer rates. This results in low bed temperatures, but NO_x is still produced from fuels containing organically bound nitrogen. If this technique is shown to be attractive on a cost-effectiveness basis, means of reducing NO_x emissions from fluid bed combustion should be sought.

In summary, combustion modification techniques for NO_x control show a high technical potential. The cost of implementation of such techniques is not expected to be excessive, based on the relative simplicity of the approaches considered. (Detailed cost and cost-effectiveness evaluations will be presented in Section 8 and 9 of this report.) From the technical standpoint, the broad-based applicability of these methods to different types of combustion equipment fired with different types of fossil fuels (particularly in the case of coal) remains to be defined.

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5. CONTROL OF NO_x EMISSIONS BY COMBUSTION FLUE GAS TREATMENT

5.1 GENERAL CONSIDERATIONS

Removal of the nitrogen oxides from flue gas provides an alternate method for controlling combustion related emissions. The typical composition of flue gases obtained from the combustion of fossil fuels is shown in Table 5-1.

Table 5-1

Typical Compositions of Flue Gases

Component	Volume % Combustion of Coal[a]	 Oil[b]	 Gas[c]
N_2	76.2	77.0	72.3
CO_2	14.2	12.0	9.1
H_2O	6.0	8.0	16.8
O_2	3.3	3.0	1.8
SO_2	0.2	.15	--
NO_x	.07[d]		
Particulates grams/ft^3	0.5[e]	0.01	--

a. Calculated for burning with 20% excess air a typical high volatile bituminous coal of the following composition: carbon-70.1%, oxygen-6.6%, hydrogen-4.9%, nitrogen-1.4%, sulfur-3.0%, ash-12.7%, H_2O-1.3%

b. Calculated for burning a typical residual fuel oil of the following composition: 86.5% carbon, 10.3% hydrogen, 2.5% sulfur, 0.7% nitrogen with 20% excess air.

c. Calculated for burning natural gas with 10% excess air.

d. This is an average value. Actual values range from .02 to .15%.

e. Assumes 90% particulates removal.

Eight different oxides of nitrogen are known: N_2O, NO, $(NO)_2$, N_2O_3, NO_2, N_2O_4, N_2O_5 and NO_3, but combustion gas analyses indicate that only two of these oxides, NO and NO_2, are present in any significant amounts in the flue gases. The colorless oxide NO is formed at the high temperatures existing in or near the combustion zone. As the combustion gases cool, the NO is oxidized by elemental oxygen to the reddish brown NO_2. This oxidation is so slow that at the stack outlet, only a few percent of the total nitrogen oxide emissions are NO_2.

Although the concentrations of nitrogen oxides in flue gases are low, the volumes of gas emitted by large sources such as power plants are so great that individual plants may release significant amounts of these contaminants. The NO_x emissions shown in Table 5-2 reflect the observation that large gas fired boilers tend to produce more NO_x per unit of fuel burned than do their equivalent coal fired counterparts, whereas the reverse is generally true for small boilers.

Table 5-2

Quantities of Gases and Nitrogen Oxides Emitted by Typical Power Plants

Power Plant	Volume of Gases Released, 10^6 SCFH	Lbs/Hr NO_x Released (Calculated as NO_2)
750 MW Gas Fired	73	9500
750 MW Coal Fired	83	7300
250 MW Gas Fired	29	1200
250 MW Coal Fired	32	2500

Processing large volumes of gas such as these for NO_x control presents formidable engineering problems in gas contacting, equipment size, pressure drop, temperature control, etc. In addition to these general problems, the control of nitrogen oxides presents many specific and difficult problems because of their low concentration, their chemical and physical properties, and the interfering action of other species present in stack gases. Moisture, carbon dioxide, sulfur dioxide, and oxygen are present in greater concentrations than the nitrogen oxides. These will prevent the use of certain sorption, scrubbing and catalytic processes or at least make their use much more difficult. Particulates present similar problems. Nevertheless, a number of existing and potential stack gas emission control processes have been identified.

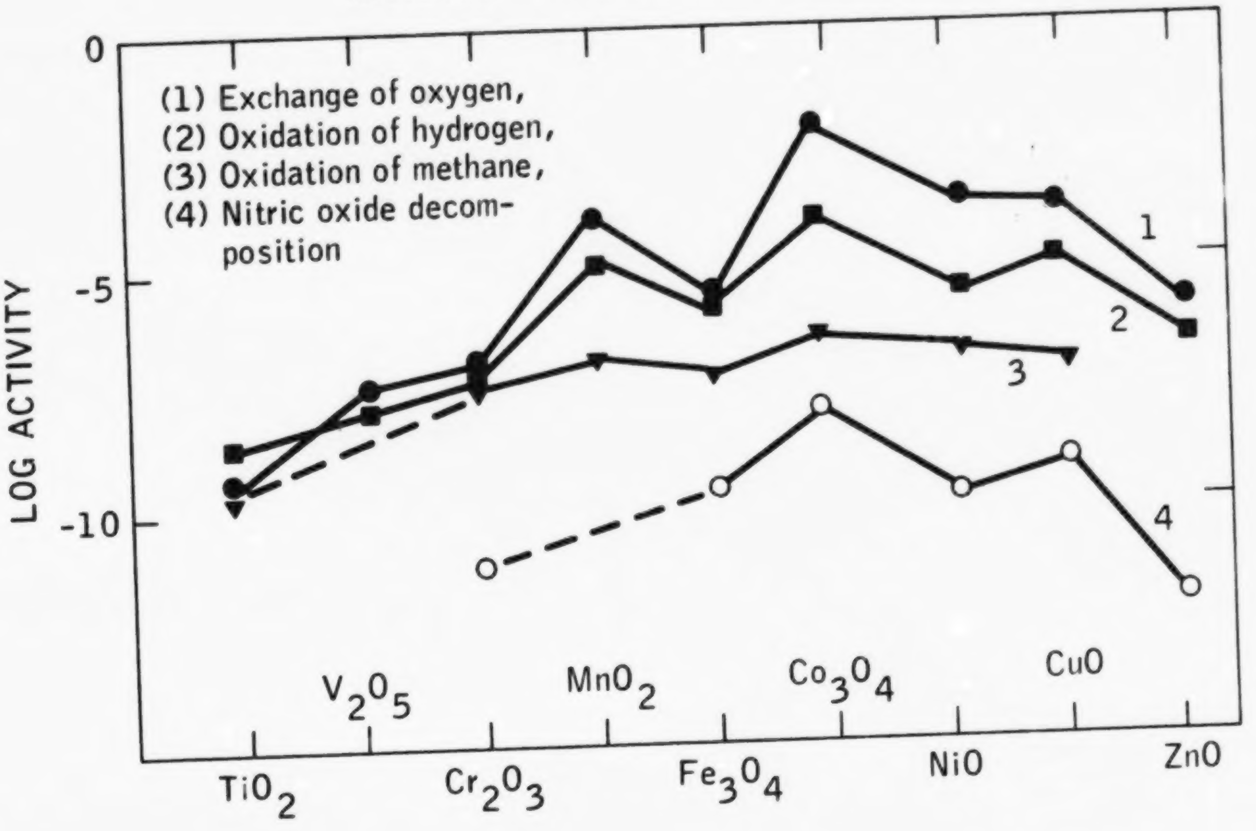
In Sections 5.2 to 5.7, catalytic decompositions, catalytic reduction, adsorption, absorption and physical separations are discussed as categories of potential NO_x emission control technology. Potential control processes are outlined and general cost considerations are discussed. The most promising flue gas control processes are evaluated on a cost bases in Section 8.2 and then rated on a cost effectiveness basis in Section 9.1.

5.2. CATALYTIC DECOMPOSITION OF NO_x

Because of its potential simplicity, the catalyzed decomposition of nitrogen oxides to nitrogen and oxygen has obvious advantages as a control technique. As pointed out in Section 4.1., this decomposition is favored at all but very high temperatures. The fact that nitrogen oxides do not revert back to their elements as stack gases cool is due to the fact that decomposition is very slow, even when catalyzed. Shelef, Otto and Gandhi (5-1) cite Boreskov's comparisons of the catalyzed NO decomposition to the oxidation of methane and hydrogen. This comparison, reproduced in Figure 5-1. shows that the rate of NO decomposition is one to two orders of magnitude slower than the very slow oxidation of methane and by several orders of magnitude slower than the oxidation of hydrogen.

Figure 5-1

COMPARISON OF CATALYTIC ACTIVITY FOR VARIOUS REACTIONS MEASURED BY BORESKOV



Another indication of the slowness of the NO decomposition reaction is the very long-lived experiment of Howard and Daniels (5-2). In 1917, they sealed NO in tubes with a wide assortment of catalysts maintained at room temperature. Fifty years later, no detectable decomposition was observed.

A number of investigators have studied the kinetics and mechanism of NO_x decomposition and have obtained different results. Green and Hinshelwood (5-3) investigated the decomposition on a heated platinum wire. Over the temperature range of 1000 to 1500°C, they determined the reaction to be unimolecular, unaffected by nitrogen but retarded by oxygen. Bachman and Taylor (5-4), who carried out the decomposition over platinum-rhodium, also found the decomposition to be retarded by oxygen, but bimolecular with respect to nitric oxide. Vetter (5-5) studied the decomposition of nitrogen oxides in a flow system between 927 and 1627°C and found a catalytic effect of oxygen on the reaction. Wise and Frech (5-6, 5-7) in their studies concluded that the thermal decomposition of nitric oxide was predominantly heterogeneous and unimolecular below 1000°K and homogeneous and bimolecular above 1400°K. They observed a similar catalytic effect of oxygen as had Vetter and explained it on the basis of a chain reaction mechanism involving oxygen atoms reacting in the initial step with NO. Kaufman and Kelso (5-8) and later Yuan, et al., (5-9) disputed this contention of oxygen enhancing the reaction. Yuan and coworkers also observed the reaction to be heterogeneous and zero order below 1100°C and homogeneous and bimolecular above 1800°C. Fraser and Daniels (5-10) measured the decomposition of 10% NO in helium at temperatures ranging from 740 to 1040°C on Al_2O_3, CaO, Cr_2O_3, Ga_2O_3, ZrO_2, Fe_2O_3, TiO_2, and ZnO catalysts. They found the decomposition to be zero order in this temperature range and obtained the rates shown in Table 5-3.

Table 5-3.

Rates of Decomposition of NO at 1040°C

Catalyst	Zero Order Rate of Decomposition (g moles/liter/sec/gr. cat)
Ga_2O_3	198.0×10^{-6}
Al_2O_3	94.8×10^{-6}
CaO	32.3×10^{-6}
ZrO_2	5.5×10^{-6}
Cr_2O_3	5.4×10^{-6}
Fe_2O_3	0.9×10^{-6}
ZnO	0.7×10^{-6}

The decomposition of NO, diluted in some cases with helium, was also studied by Shelef, Otto and Gandhi (5-1). The catalysts evaluated in this study are shown in Table 5-4. along with the measured reactivities.

Table 5-4

Catalyst Performance

Catalyst	Chemical Analysis (Wt %)	Surface* Area (m^2/g)	Temperature Range (°C)	Activation Energy (kcal/mole)	Reaction Order		Decomposition Rate at 500°** (Moles/(m^2 x min) x 10^{10})
					Measured (at °C)	Assumed	
Al_2O_3-SiO_2 Support	95 Al_2O_3, 5 SiO_2	204	548-716	25.9	0.8 (750)	1	2.67
Supported Cobalt Oxide	8.1 Co	175	402-709	22.5	1.2 (654)	1	16.2
Supported Cobalt Oxide	10.1 Co	206	434-585	14.2	0.75 (572)	1	45.4
Supported Cobalt Oxide Doped With Chromium	9.77 Co 0.14 Cr	197	419-752	17.0		1	37.6
Doped With Lithium	9.00 Co 0.13 Li	136	443-761	19.4		1	47.2
Doped With Lithium	7.64 Co 0.02 Li	187	440-740	18.1		1	55.0
Supported Platinum	3.72 Pt	231	386-532	20.1	0.95 (504-532)	1	74.8
Supported Copper Chromate	5.75 Cu 4.96 Cr	175	496-699	10.6	0.88 (579)	1	116
Supported Copper Chromate	2.46 Cu 3.75 Cr	183	424-737	14.4	1.09 (533)	1	48.7
U.O.P.	--	153	393-761	13.2	0.3-0.45 (532-645)	1/2	147
Copper Oxide on Silica	29 Cu	21.5	661-938	33.2	1.2 (501)	1	2.98
Cobalt Oxide on 5A Sieve	4.6 Ca	359	399-498	23.2		1	37.1
Unsupported Co_3O_4		8.0	279-368	28.3		1	95,420

* After use.

** At constant NO concentration as given at inlet ($p = 1$ atm, $T_o = 25°C$).

Over the temperature range from 300 to 900°C. most of the measured orders of reaction were close to one. Unsupported Co_3O_4 proved to be the most active catalyst when tested on pure NO. Since the problem of decomposing NO present in stack gases is very different from the decomposition of pure NO or NO diluted with helium, extrapolation of the results to control of stack gas emission is unwarranted.

Comparatively little published work is available on decomposition of nitric oxide when present in low concentrations as is the case for flue gases. Sakaida, et al. (5-11), studied the decomposition of NO at a concentration of about 4000 ppm in nitrogen, on alumina pellets impregnated with either .1% platinum oxide or 3% nickel oxide. In the range of 800 to 1000°F and a pressure range of 1 to 15 atmospheres, the reaction was found to be second order with respect to nitric oxide, retarded by atomic oxygen and further retarded by excess nitrogen. Sourirajan and Blumenthal (5-12) investigated the decomposition reaction with 300 to 2100 ppm nitric oxide diluted with nitrogen over cobalt and copper oxide supported catalysts at temperatures in the range of 300 to 1000°C. In contrast to the work of Shelef, Otto and Gandhi (5-1), copper oxide deposited on silica gel was found to be the best catalyst. With this catalyst, 69% NO decomposition was obtained at 950°F and a low space velocity of 1320 V/V/Hr from a gas containing 892 ppm NO in N_2. Other supports investigated were kieselguhr and alumina.

The most extensive screening study of NO decomposition catalysts for which results have been published is that by Riesz, et al.(5-13) at the Illinois Institute of Technology's Research Institute (IITRI). In this study, 21 commercial catalysts and 17 laboratory-prepared alumina supported catalysts were evaluated using a gas mixture containing 2000 ppm NO in N_2. The results of this work, summarized in Tables 5-5, and 5-6 indicated little or no reaction in all cases at the high space velocities used (i.e., about 120,000 V/V/Hr).

Table 5-5

Results of IITRI's Study of Nitric Oxide Decomposition Catalysts - Commercial Catalysts

		Decomposition Temperature, °F					
		932		1112		1292	
Catalyst	Catslyst Manufacturer	SV(a)	% NO Decomp.	SV	% NO Decomp.	SV	% NO Decomp.
Magnesia-alumina spinel (27-70%)	Norton, LMA-520	1880	3	2075	4		
Silica-alumina (88-12%)	Universal Oil Products	1490	4				
Silica-phosphoric acid (70-30%)	Universal Oil Products, No. 2	1940	0	2025	0		
Vanadia-silica potassium sulfate (10-65-23%)	Davison Chemical, 903	1825	0	1785	0	1785	0
Vanadia-alumina (7-93%)	Harshaw Chemical, V-X-L533	38	20				
Hopcalite	Mine Safety Appliances	1450 135	0 0				
Chromia-alumina (19-81%)	Harshaw Chemical CR-0205	1955	0	2140	0	2100	0
Ferric oxide	Girdler G3, carbon monoxide shift	1930*	2				
Magnetite	Tennessee Valley Authority, Ammonia synthesis	2000	0				
Nickel oxide ($NiO-SiO_2$)	University Oil Products, hydrogenation	1820	7	1935	3		
Cobalt-molybdate ($Co-MoO_3-Al_2O_3$)	Harshaw Chemical, Co-Mo-0401 desulfurization	1840 930	0 0				
Copper oxide-alumina (10-90%)	Harshaw Chemical, Cu-0801	1255	3	1670	0		
Zinc oxide (99%)	Harshaw Chemical, Zn-0401	1870	0	1870	5		
Mossy zinc	Baker	2140	4	2045	2		
Molybdena-alumina (10-90%)	Harshaw Chemical, Mo-1202	1795	7				
Palladium-alumina (0.5-99.5%)	Baker	1900	1	1550	3	1910	1
Silver oxide-alumina (20-80%)	Harshaw Chemical, Ag-0301	1635	0	1620	0	1430	0
Tungstic oxide-alumina (10-90%)	Harshaw Chemical, W-0101	1680	0				
Platinum-asbestos (5-95%)	Baker	2000	18	2000	10	2140	7
Platinum-alumina (0.5-99.5%)	Baker	1770	5	2080	0	2085	0
Platinum-alumina (0.6-99.4%)	Baker, dehydrogenation	2140	0	1770	0	1890	0

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* 250°C.

(a) Volumes of gas per minute per volume of catalyst.

Table 5-6

Results of IITRI's Study of Nitric Oxide Decomposition Catalysts - Laboratory-Prepared Catalysts

			Decomposition Temperature, °F					
			932		1112		1292	
Catalyst	Oxide	Alumina*	SV	% NO Decomp.	SV	% NO Decomp.	SV	% NO Decomp.
Sodium oxide-alumina	10	90	1835	1	1970	0	1835	1
Potassium oxide-alumina	5	95	1840	3	1815	0	1820	0
Potassium oxide-alumina	15	85	2250	2	2090	1	2045	1
Chromium oxide-alumina	10	90	1835	0	1870	0	2060	0
Manganese oxide-alumina	10	90	2045	0	1685	0	2130	0
Iron oxide-alumina	10	90	1690	0	2000	0	2090	0
Cobalt oxide-alumina	10	90	1860	0	1860	0	1955	0
Nickel oxide-alumina	10	90	1575	2	1685	2	1815	3
Copper oxide-alumina	10	90	1605	0	1635	0	1550	5
Zinc oxide-alumina	10	90**	1955	1	2090	1	2140	1
Strontium oxide-alumina	10	90	1910	0	1585	0	1585	0
Silver oxide-alumina	10	90	1665	0	1815	0		
Cadmium oxide-alumina	10	90	1740	0	2205	0	2220	0
Barium oxide-alumina	2.5	97.5	2140	0	1845	0	1955	0
Lead oxide-alumina	5	95	1940	0	1845	4	1860	5

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* Harshaw Chemical, Al-0401.

** Alcoa, XH-151.

Under a NAPCA grant, Walling (5-14) has studied the decomposition of nitric oxide by a number of commercially produced catalysts at 300, 600, and 800°F and at a space velocity of about 3400 V/V/Hr. He has used a SO_2-free simulated flue gas containing 500 ppm NO, and 3% O_2. The catalysts he has tested to date are shown in Table 5-7.

Table 5-7.

Decomposition Catalysts Evaluated by Walling

Harshaw V_2O_5 Catalyst (V-0301)
Harshaw CuO Catalyst (Cu 0803)
Harshaw Mo_2O_3 Catalyst (Mo 1202)
Girdler Ba-Promoted $CuCr_2O_4$
Girdler $CuCr_2O_4$
Girdler Cr-Promoted Fe_2O_3
Girdler NiO Catalyst (H-219)
Fisher Reagent Co_3O_4
Fisher Reagent Fe_2O_3
Fisher Reagent MnO_2
Fisher Reagent CeO_2
Baker 5% Platinum on Asbestos

Walling's results indicate that these materials have little effect on the NO level of the gas at 300 and 800°F. At 600°F, the NiO, Co_3O_4 and platinum asbestos showed initial NO removal, but this removal falls off to zero with continued use. This indicates that the initial removal observed may be due to a surface sorption or reaction rather than true NO decomposition.

Wikstrom and Nobe (5-15) have also studied the decomposition of nitrogen oxides in the presence of oxygen. Using copper oxide supported on alumina, they reported being able to decompose as much as 50% of 1260 ppm NO_2 to nitrogen and oxygen at a space velocity equivalent to about 350 SCFH/lb catalyst at a temperature of 970°F. Attempts by researchers at Esso Research to reproduce these experimental data, however, have met with no success.

Catalyst testing with actual flue gas was carried out by Haagen-Smit at Southern California Edison's El Segundo Power Station. In searching for flue gas desulfurization and NO_x decomposition catalysts, Haagen-Smith evaluated over twenty different materials (shown in Table 5-8.) using actual power plant flue gas from which only particulates had been removed. Of the materials tested, only copper oxide showed promise as a decomposition catalyst, providing a little more than 10% decomposition at test conditions (5-16).

Table 5-8.

Catalysts Evaluated at Southern California Edison Co.

	Temp., °F	Space Vel. ft^3/hr/gr. cat.
Harshaw Activated Alumina - AL 0104T	150-1400	.06
Harshaw Chrome-Alumina - CR 0205	350-1500	.06
$Cr(NO_3)_3$ on Harshaw - AL 104T	200-1600	.05
Chromic Oxide on Berl Saddles	350-1400	.02
Copper Wire	600-1350	.09
Copper Oxide (CuO)	450-1350	.04
Copper Chromite on		
- Berl Saddles	Unavailable	
- $MgO-Al_2O_3$ Spinel	Unavailable	
Ferric Chloride on Ceramic Support	Unavailable	
Steel Wool	600-1400	.02
Linde Mol. Sieves 4A 5A 13X	150/700	.06-.15
Sodium 2-Phosphate-18-Molybdate on Alundum	500-1200	.08
Harshaw Molybdenum Alumina MO 1207	300-1300	.06
UOP NiO_2-SiO_2 Hydrogenation Cat.	200-1000	.04
Houdry Platinum	400-500	.05
KNO_3 on Alundum	350-1250	.09
$NaNO_3$ on $MgO-Al_2O_3$ Spinel	200-1200	
Harshaw Vanadium VO5015	500-1350	.06
Monsanto Vanadium	700-1100	.12

In other studies CaO (or its product with SiO_2, i.e., $CaSiO_4$), has shown promise of promoting NO decomposition in an actual combustion-flue gas environment. Working under an agreement with NAPCA, Argonne National Laboratory has shown (5-17) that the injection of finely sized limestone into a fluidized bed of combusting coal to capture SO_2 also reduces the NO emissions. Operating at a temperature of 1600°F, the injection of -325 mesh limestone into a -6 mesh bed of coal at a stoichiometric ratio of 1.3 to 1.7 CaO/S decreased NO emissions from 550 to about 410 ppm at a gas-solids contact time of about three seconds. In other fluidized bed combustion studies, Zielke et al. (5-18) report NO emissions of 60 to 340 ppm when combusting finely sized chars and coal in coarse beds of dolomite. In these studies, combustion was carried out at 1800°F and 8 psig pressure with gas-solids contact times of under two seconds. Although NO concentration without the dolomite is not reported, it is expected that it should be about 500 ppm based on the fluidized bed combustion work of others.

Besides CaO, other alkaline earth metal and alkaline metal oxides and silicates catalyze the decomposition of NO. Peters et al. (5-19) report that a mixture of barium oxide, calcium oxide and strontium oxide gives over 95% decomposition of NO_2 to N_2 and O_2 at temperatures of about 1500 to 1650°F and hourly space velocities of about 200. At 1650°F, a sodium silicate (Na_4SiO_4) catalyst gave 94% decomposition at an hourly space velocity of about 300.

The use of inexpensive additives such as limestones, dolomites, and calcium and sodium silicates in a fluidized bed combustion system appears to offer the best possibility for NO_x emission control by catalytic decomposition and simultaneous removal of sulfur oxides by chemical reaction. A system employing pulverized coal and coarse additive may yield better results than one using coarse coal with fine additive. In the former system, the hold up of additive in the fluidized bed is larger. This gives NO molecules a greater opportunity to find active surface. Furthermore, combustion of injected coal should be completed closer to the bed inlet giving the NO formed greater opportunity to contact catalyst.

5.3. CATALYTIC REDUCTION OF NO_x

The reduction of nitrogen oxides can be classified as either selective or non-selective. In the former, NO is preferentially reduced in the presence of oxygen. In the latter case, the oxygen must first be consumed before the NO reduction will take place. Selective reduction is preferred as a control technique to minimize reductant requirements.

5.3.1 Non-Selective Reduction

Non-selective catalytic reduction is already being used in a number of nitric acid manufacturing plants for nitrogen oxides emission control. Two types of reduction are practiced in these plants - decolorization and abatement. Decolorization involves reducing NO_2 to colorless NO and is accompanied by the reduction of some oxygen. In non-selective abatement, all nitric oxides are reduced to nitrogen by using sufficient fuel to consume all the oxygen. With the non-selective abatement, some CO is formed and released to the atmosphere when using carbon containing fuels (5-20).

Methane and hydrogen are typically used as fuels for the reduction. The reactions which take place with methane are:

$$CH_4 + 4NO_2 \longrightarrow 4NO + CO_2 + 2H_2O \qquad (5\text{-}1)$$

$$CH_4 + 2O_2 \longrightarrow CO_2 + 2H_2O \qquad (5\text{-}2)$$

$$CH_4 + 4NO \longrightarrow 2N_2 + CO_2 + 2H_2O \qquad (5\text{-}3)$$

Similar equations apply to reduction with hydrogen but four moles of hydrogen are required to replace one mole of methane.

The non-selective reduction reactions are highly exothermic resulting in temperature rises of 230°F per % oxygen reduction using methane and 270°F per % oxygen reduction using hydrogen. With noble metal catalysts, minimum inlet temperatures to assure ignition are about 850°F for methane and 400°F for hydrogen.

Supported platinum and palladium catalysts are both used for decolorization and non-selective abatement in HNO_3 plants. Minimum ignition temperatures are lower with palladium, while platinum will withstand higher temperatures. Some of the catalyst supports used include ceramic honeycomb, ceramic spheres or pellets, and woven Nichrome ribbon.

Comparatively little information is available on the use of non-noble metal catalysts for non-selective NO reduction in stack gases. The use of nickel on alumina and silica (5-21) has been described for tail gas NO_x reduction with natural gas. In a separate reference (5-22), nearly complete reduction of nitric oxide by hydrogen has been claimed with 75% nickel oxide on alumina at temperatures of 550-750°F and space velocities in excess of 50,000 V/V/Hr. Presumably, some of the catalyst systems researched for automotive use could be used for stack gas emission control. Table 5-9 lists some of the systems studied to date for automotive exhaust control and the results obtained.

Table 5-9.

NO_x Reduction Catalysts Studied For Automotive Emissions Control

		Catalyst		Experimental Conditions				
Investigator(s)	Reaction	Type	Pre-Treat	Temp.	NO Conc.	Space Vel.	% Conv.	Poisons
Baker & Doerr (5-23)	$2NO+2CO \rightarrow N_2+2CO_2$	Harshaw CuO-203 82 $CuO \cdot 17\ Cr_2O_3$	Reduction	120-270 °C	1500 ppm 1% CO in N_2	8-36,000 $Hr.^{-1}$	10-100	No data
Roth & Doerr (5-24)	$2NO+2CO \xrightarrow{N_2} N_2+2CO_2$	$CuCr_2O_4$ $Ba \cdot CuCr_2O_4$	Reduction	100-250 °C	400 ppm 6% CO in N_2	10,000 $Hr.^{-1}$	10-100	No data
Ayen & Peters (5-25)	$2NO+2H_2 \xrightarrow{N_2} N_2+2H_2O$ $2NO+5H_2 \xrightarrow{N_2} 2H_2O+2NH_3$	10% Cu 29% Zn 31% Chromia Girdler G-50		375-425 °C	1 to 5%	7,000-10,000 $Hr.^{-1}$		No data
Sourirajan & Blumenthal (5-12)	$\left.\begin{matrix} NO \\ \& \\ NO_2 \end{matrix}\right\} + \begin{matrix} CO \\ or \\ H_2 \end{matrix} \rightarrow \begin{matrix} N_2 \\ NH_3 \end{matrix}$	30 $CuO \cdot 70\ SiO_2$	Reduction	100-500 °C	500-800	7,000-10,000 $Hr.^{-1}$	30-100	No data
F. R. Taylor (5-26)	$\left.\begin{matrix} NO+CO \\ or\ H_2 \end{matrix}\right\} \xrightarrow[N_2]{He} N_2$	Zinc Cu Chromite iron chromite Ba-Cu chromite copper chrome alumina		200-320 °C	400-6000 ppm NO 6% CO	15,000-25,000 $Hr.^{-1}$	20-100	Limited Data
Brennan (5-27)	Presumably $2NO+2CO \rightarrow N_2+2CO_2$	Alkali & alkaline earth crystalline SiO_2-Al_2O_3	N_2	400-600 °C	1000		10-95	No data
Baker & Doerr (5-28)	$2NO+2CO \rightarrow N_2+2CO_2$	62 $CuO \cdot 5\ Co_2O_3$ 33 Al_2O_3	Catalyst in reduced state	450°C		10,000 $Hr.^{-1}$	High	400 Hrs. on commercial leaded gasoline

For stationary combustion sources, NO_x emission control by nonselective reduction would be best carried out by running the combustion at stoichiometric or substoichiometric air/fuel conditions. Otherwise, reductant requirements would be prohibitive. Thus for example, complete oxygen burnout in a typical flue gas containing about 3% O_2 would require the addition of the equivalent of 15 to 20% of the power plant fuel as reductant. Under stoichiometric or substoichiometric conditions, on the other hand, there would be little or no oxygen and the CO formed would be available for reduction of the nitrogen oxides. Ryason and Harkins (5-29), who have studied such reduction under simulated conditions, have shown that it can be used to remove both sulfur oxides and nitrogen oxides simultaneously from combustion gas. Using a copper on alumina catalyst at space velocities of about 10,000 V/V/Hr and temperatures of about 1000°F, nearly complete reduction of both SO_2 and NO were obtained from a simulated combustion gas containing CO in slight excess of that needed for the reduction. The reaction of SO_2 with CO initially results in the formation of sulfur. With excess CO, however, the sulfur reacts further to form COS. Thus, the CO concentration would be very important in such a process, and this means the air/fuel ratio for the combustion would have to be very closely controlled.

Table 5-10.

Ryason's and Harkin's Data For Simultaneous
Reduction of SO_2 and NO by Catalyzed Reaction With CO:
Copper Oxide-on-Al_2O_3 Catalyst, 1000°F, Reactants in N_2

SO_2, %	CO, %	CO_2, %	Approximate NO_x, Conc.	Residence Time, Sec	Percent Reduction SO_2	Apparent Percent Reduction NO_x
0.47	1.3	8	125	0.57	98	78-100
0.47	1.3	8	125	0.46	98	31-100
0.47	0.97	5.8	160	0.57	95	100

5.3.2. Selective Reduction

5.3.2.1. Reduction By Hydrogen or Carbon Monoxide

A selective reduction process for NO control would have the advantage of permitting conventional excess air operation of the boiler avoiding potential emission of CO and smoke and the danger of explosion. In such a process, a reducing gas, preferably H_2 (to avoid CO pollution by unreacted reductant) would be added to the flue gas in controlled amounts sufficient for reaction with the NO.

Shelef has reported (5-30) results obtained on a series of catalysts evaluated for promoting selective reduction of NO by CO. Table 5-11. summarizes the results he obtained comparing reactions (5-4) and (5-5) with reaction (5-6).

$$2NO + CO \rightarrow N_2O + CO_2 \quad (5\text{-}4)$$

$$N_2O + CO \rightarrow N_2 + CO_2 \quad (5\text{-}5)$$

$$O_2 + 2CO \rightarrow CO_2 \quad (5\text{-}6)$$

The temperature for 50% removal was used as an index of reactivity. Of the catalysts tested, only supported Fe_2O_3 and Cr_2O_3 showed lower temperature and faster CO-NO reaction than CO-O_2 reaction. At low temperatures, N_2O was observed to be the sole reaction product of the CO-NO reaction while at the high temperature the reduction proceeded all the way to N_2.

Table 5-11

Relative Effectiveness of Supported Catalysts For the CO-NO and CO-O_2 Reactions

Supported Catalyst	Temperature (°C) of 50% CO Removal CO-NO	 CO-O_2
Fe_2O_3	145	180
$CuCr_2O_4$	155	115
Cu_2O	175	140
Cr_2O_3	220	265
NiO	250	220
Pt	285	215
Co_3O_4	350	115
Bare Support	425	365
MnO	435	195
V_2O_5	560	405

Flow rate 1400 cc/min, catalyst volume 80 cc.

Inlet gas composition in CO-NO reaction ~ 1.2% CO; 2% NO.

Inlet gas composition in CO-O_2 reaction ~ 1.2% CO; 1.2% O_2.

Using the Cr_2O_3 catalyst, Shelef found that the $CO-O_2$ reaction predominates over the CO-NO reaction in gas mixtures containing NO, CO and O_2, and that average oxidation state of the chromium oxide surface in the absence of oxygen is lower than in the presence of oxygen. Comparable data for NO, CO and O_2 system over the Fe_2O_3 catalyst were not reported. However, a recent paper (5-31) indicates that a catalyst system containing iron oxide has been found by Shelef to promote the selective reduction of NO by hydrogen at temperatures below 180°C. The catalyst is subject to sulfur poisoning and is not effective with CO.

5.3.2.2. Reduction with Ammonia

The ability of ammonia to reduce NO selectivity has long been recognized. Neumann and Rose (5-32), while studying the catalytic oxidation of ammonia to nitric acid concluded that the nitrogen formed during oxidation was the result of ammonia reacting with nitric oxide. These researchers cite the work of Reinders and Cats (5-33) who also considered the nitrogen formed to be due to the reaction between ammonia and nitric oxide. Michailova (5-34) studied the kinetics of the reaction between ammonia and nitric oxide on the surface of a platinum filament. She found the reaction proceeded according to the stoichiometric equation: $6NO + 4NH_3 \rightarrow 5N_2 + 6H_2O$ and the rate was independent of the pressure of NO and NH_3 but dependent on their ratio. Michailova concluded that the reaction proceeded between adjacently adsorbed molecules on the platinum surface and on this basis derived a rate equation:

$$\frac{d(NO)}{dt} = \frac{P_{NH_3} \; P_{NO}}{(\alpha P_{NH_3} + \beta P_{NO})^2} \qquad (5\text{-}7)$$

where α and β are constants and P is reactant partial pressure.

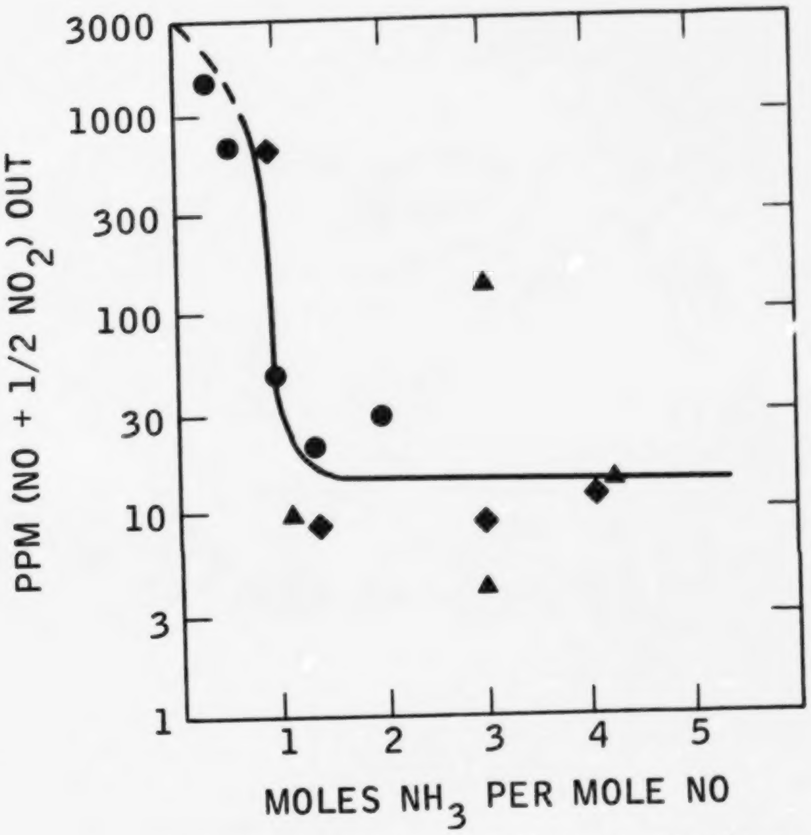
Thermodynamically, the reactions between NO_x and NH_3 are indicated to be very favorable. Temperatures for these reactions should be controlled within the range of 400°F to 600°F, since ammonium nitrate is formed below 400°F and ammonia is oxidized to NO_x at higher temperatures.

	Δ F-Kcal/g Mole NO_x @ 440°F	
$6NO + 4NH_3 \longrightarrow 5N_2 + 6H_2O$	-73.2	(5-8)
$6NO_2 + 8NH_3 \longrightarrow 7N_2 + 12H_2O$	-121.5	(5-9)

A control process using NH_3 with platinum group metal catalysts to reduce the NO emitted by nitric acid manufacturing processes is described by Cohn, Steele and Andersen (5-35). Andersen, Green and Steele (5-20) present data on the selectivity of NH_3 for reducing NO. These data are shown in Figure 5-2.

Figure 5-2

SELECTIVE REDUCTION OF NO_x BY AMMONIA



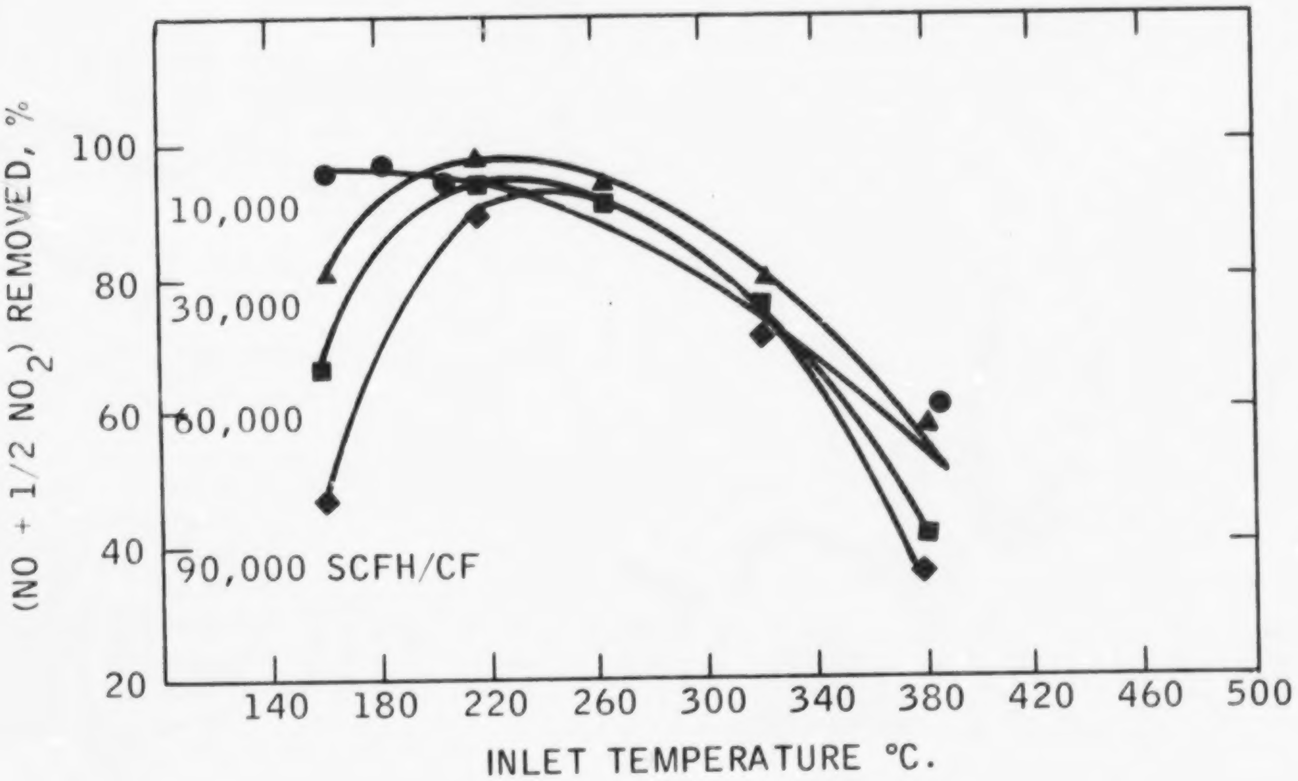
Catalyst, 0.5% Pt. on 1/2-inch Cylinders

	◆	▲	●
% NO	0.28	0.28	0.30
% O_2	3.4	3.4	3.0
% H_2O	0	1.6	0.66
% N_2	Balance	Balance	Balance
Catalyst volume, ml.	10	10	400
Inlet temp., °C.	149-166	149-166	163-180
Pressure, psig.	0	0	100

With the addition of only one mole of NH_3 per mole of nitric oxide, to a gas containing about ten moles of O_2 per mole of NH_3, the platinum catalyst used was sufficiently selective to reduce the NO concentration from 3000 to 30 ppm. Andersen, et al., also report the effect of temperature and space velocity on the completeness of the reaction. Their data are reproduced in Figure 5-3.

Figure 5-3

EFFECT OF SPACE VELOCITY AND TEMPERATURE ON AMMONIA REDUCTION OF NO_x



Catalyst: 0.5% Pt on 1/3-in. cylinders, in 1.76 in. dia. reactor. 100 ml. catalyst used in 30,000-90,000 SCFH/CF experiments; 400 ml. for 10,000 SCFH/CF.

Inlet gas: NO, 0.3%; O_2, 3.0; H_2O, 0.8: NH_3, 0.3. Pressure, 100 psig. Average temperature rise at and above optimum removal temperature, 33°C.

Although noble metal catalysts permit operating at very high space velocities, their use limits the applicability of this process for flue gas control because platinum group catalysts are easily poisoned by sulfur. It is recommended therefore that the use of these catalysts be restricted to gases containing less than 1 ppm of sulfur compounds (5-36). This means that the process cannot be used to control NO_x emissions from combustion of sulfur bearing fuels, even when used in conjunction with a flue gas desulfurization process, since no desulfurization process could be expected to reduce the sulfur content to such low levels.

The use of non-noble metal catalyst offers a possible solution to the sulfur poisoning problem. A recent U.S. patent (5-37) claims the use of vanadium (V), molybdenum (VI) and tungsten (VI) oxides supported on alumina or silica to be effective catalysts for promoting the selective reaction of NH_3 with nitrogen oxides. Space velocities of 10,000 to 30,000 V/V/Hr and temperatures ranging from 400° to 650°F are indicated. This patent also states that the vanadium oxide catalysts "are not sensitive to sulfur." Another patent (5-38), describing the use of a catalyst consisting of 85% Fe (III) oxide, 10% Cr (III) oxide and 2% Cr (VI) oxide on silica with alkali and alkaline earth promotors, also claims the ammonia reduction of nitrogen oxides in the presence of sulfur impurities. An example of a gas composition for which the catalyst is said to be effective is given in Table 5-12. These results, however, were obtained at a very low space velocity equivalent to about only 20 Ft^3/Hr/Lb catalysts. Thus, this catalyst may not have been exposed to a sufficient volume of gas to see a sulfur poisoning effect.

Table 5-12

Gas Composition (311)

Component	Volume Percent
CO_2	6.0
O_2	8.0
N_2	86.0
SO_2	175 ppm
NO	120 ppm
NO_2	15 ppm

The use of a silica alumina supported copper oxide catalyst is claimed (5-39) to reduce the hydrocarbon, carbon monoxide and nitrogen oxide content of internal combustion engine exhaust gases when contacting the exhaust gas with oxygen and NH_3 over the catalyst. Surprisingly high temperatures in the range of 700 to 1200°F are recommended.

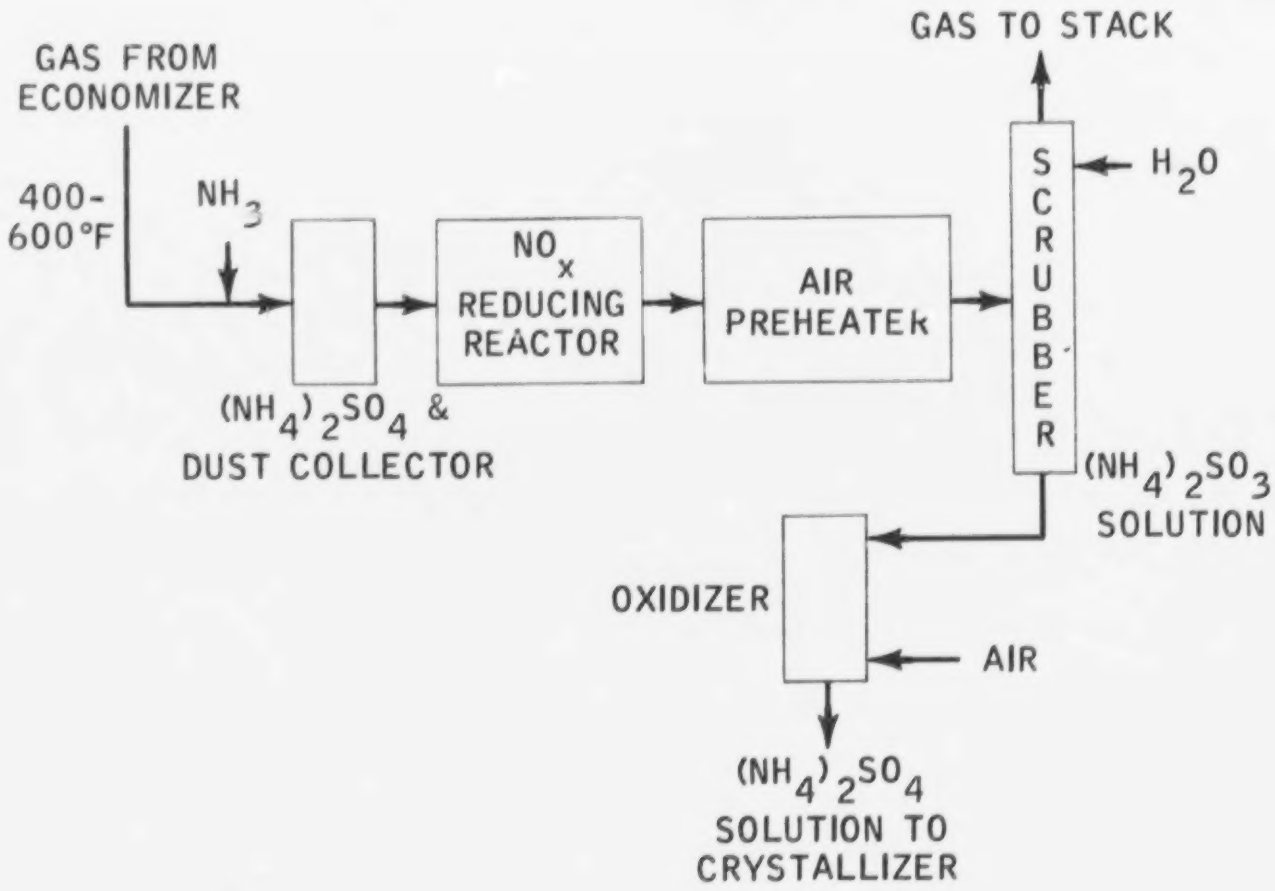
Other non-noble metal catalysts containing cobalt, nickel and iron are claimed by Anderson and Keith (5-40) to be effective at temperatures ranging from 300 to 600°F and space velocities of 3,000 to 20,000 standard V/V/Hr. No mention of catalyst poisoning is made in their patent, but Anderson has said (5-36) that all of these catalysts were found to deactivate within a matter of hours or days when used in a nitric acid plant with actual tail gas.

The low temperatures at which the NO-NH_3 reaction can be catalyzed makes NH_3 reduction a potentially attractive method of controlling NO_x emissions from power plants. Low temperature reaction permits injecting the ammonia at the outlet of the boiler or air preheater. In fact, the surface of the air preheater itself could possibly serve to support the catalyst. If a truly sulfur resistant catalyst exists or can be developed, the NH_3 reduction system could be used in coal and oil as well as gas-fired plants. The possibility would then exist of using NH_3 injection to control both the SO_x and NO_x emissions.

One example of a potential combined SO_x-NO_x control process is shown in Figure 5-4. In this process, sufficient NH_3 would be added to the flue gas to react with both oxides. NH_3 would first homogeneously react with the small amount of SO_3 present in the gas to form $(NH_4)_2SO_4$ which would be precipitated or filtered from the gas. Following the catalytic reduction of the nitric oxides, the gas would be scrubbed with water and the solution aerated to convert the ammonium sulfite solution to ammonium sulfate.

Figure 5-4

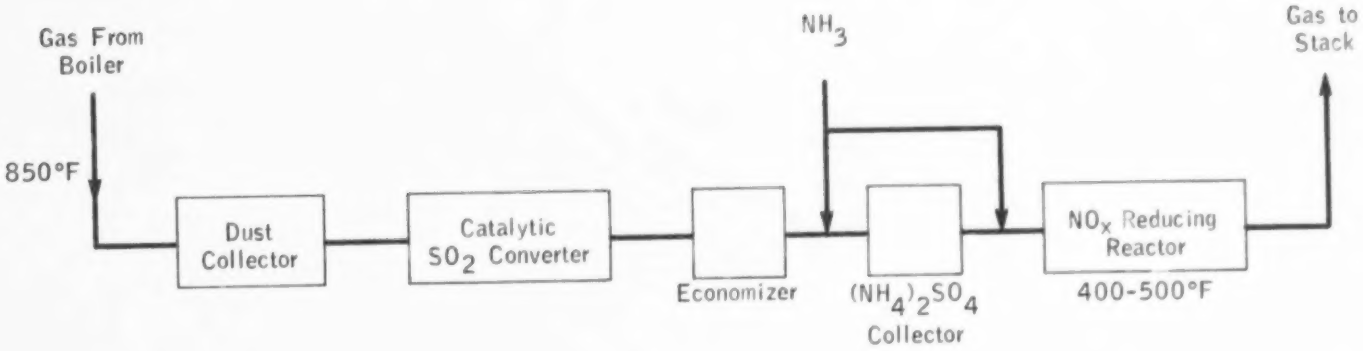
POTENTIAL PROCESS FOR SO_x-NO_x CONTROL WITH NH_3


GAS FROM ECONOMIZER
400-600°F
NH_3
NO_x REDUCING REACTOR
AIR PREHEATER
GAS TO STACK
SCRUBBER
H_2O
$(NH_4)_2SO_4$ & DUST COLLECTOR
$(NH_4)_2SO_3$ SOLUTION
OXIDIZER
AIR
$(NH_4)_2SO_4$ SOLUTION TO CRYSTALLIZER

If more complete desulfurization of the flue gas is required for the NO_x reduction, then an alternate processing scheme shown in Figure 5-5 might be used. Here, dust-free flue gas would first be oxidized as in the Kiyoura Process (5-41) to convert the SO_2 to SO_3. NH_3 injection would then remove most of the sulfur as $(NH_4)_2SO_4$ prior to reduction of the nitric oxides.

Figure 5-5

AN ALTERNATE SO_x-NO_x CONTROL PROCESS WITH NH_3



Besides NH_3, other related compounds such as hydrazine and amines are reported (5-38) to be effective for reducing nitric oxides. These are more expensive than NH_3 and appear to offer no operating advantages. Urea, which appears able to reduce nitrous acid (5-42) is likewise more expensive.

5.3.2.3. Reduction with Hydrogen Sulfide

Hydrogen sulfide may prove to be another selective NO reductant, and if so, could also be used for both SO_2 and NO emission control. The free energy change for the reaction between H_2S and NO is even more favorable than is that for the well-known Claus Process in which H_2S reacts with SO_2

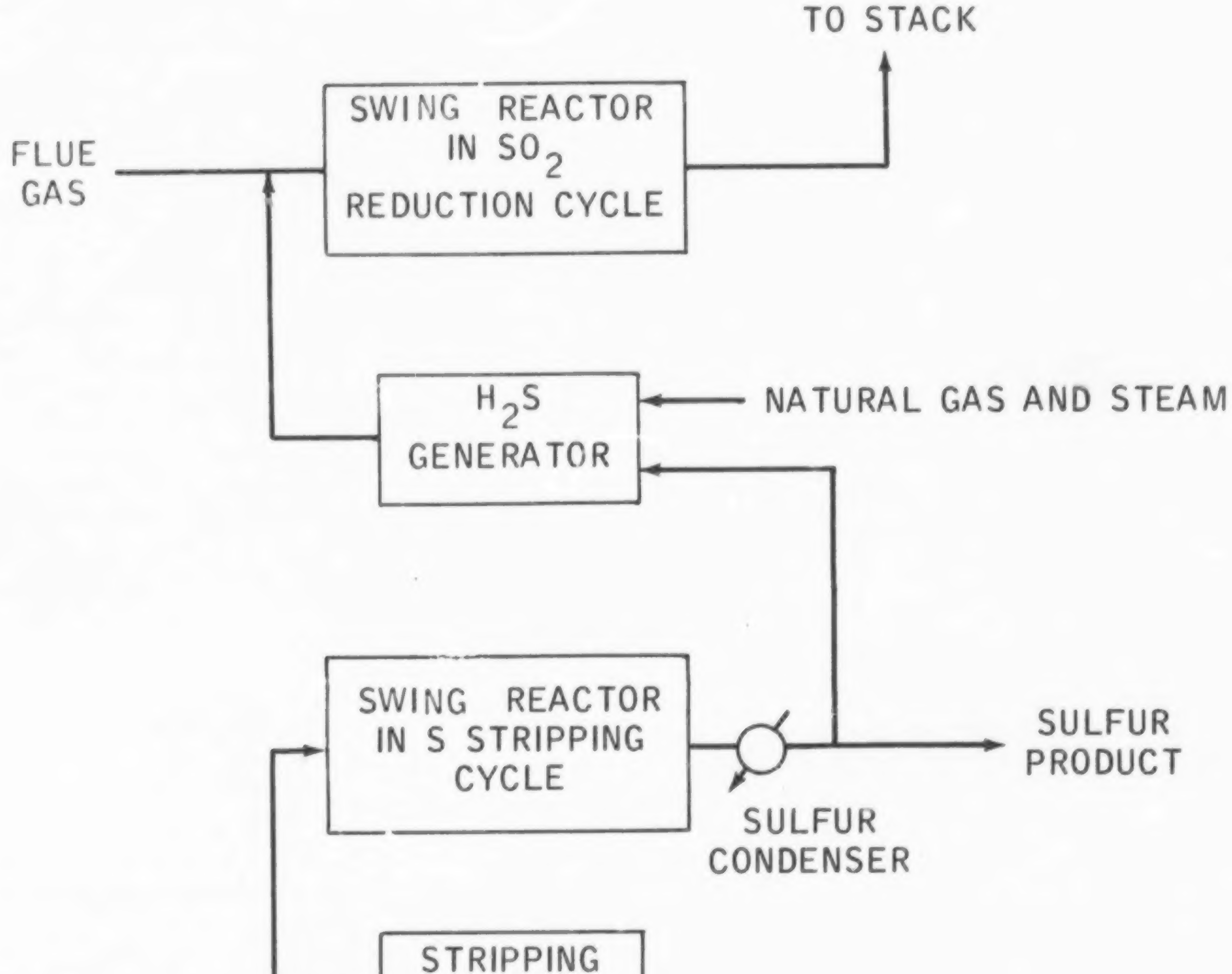
	ΔF Kcal/g Mole, 260°F	
$SO_2 + 2H_2S \longrightarrow 3S + 2H_2O$	-17.4	(5-10)
$NO + H_2S \longrightarrow S + \frac{1}{2}N_2 + H_2O$	-65.1	(5-11)

to form sulfur. The Claus reaction was proposed by Peter Spence (5-43) as the basis for a flue gas desulfurization process. More recently, Princeton Chemical Research has studied their version of this process under contract to NAPCA (PH 86-68-48).

In the Princeton Chemical Research process, a concentrated H_2S stream, produced by catalytically combusting natural gas with sulfur and steam, is recycled to the flue gas upstream of a swing catalytic Claus reactor. The catalyst used selectively promotes the reaction of H_2S with SO_2 in a flue gas containing oxygen. This selectivity enables the recycling of just enough H_2S for the SO_2 reaction. The reaction is carried out at a temperature of about 250 to 300°F so that the sulfur formed condenses on the catalyst and gradually causes it to lose activity. Periodically, the sulfur must be stripped from the catalyst at high temperature. It should be noted that in this process utilization of H_2S must be essentially 100% since H_2S is a very toxic pollutant.

Figure 5.6.

PRINCETON CHEMICAL RESEARCH
SO_2 CONTROL PROCESS


TO STACK
FLUE GAS
SWING REACTOR IN SO_2 REDUCTION CYCLE
H_2S GENERATOR
NATURAL GAS AND STEAM
SWING REACTOR IN S STRIPPING CYCLE
SULFUR PRODUCT
SULFUR CONDENSER
STRIPPING GAS GENERATOR

With synthetic flue gas containing no nitrogen oxides, Princeton Chemical Research found alumina to be an acceptable catalyst (5-44). Greater than 98% conversion was obtained until sulfur loadings on the alumina reached 25%. Contact times of 1 to 2 seconds were required at temperatures in the range of 210 to 300°F. Although stripping alone of the sulfur from the sorbent did not fully restore initial activity, it was found that this activity could be restored by passing a 5% H_2S in nitrogen stream over the alumina at about 900°F. With actual flue gas made by combusting pulverized coal, however, the activity was found to decline rapidly. This loss in activity was traced to the presence of nitrogen oxides. Preliminary evaluation of a substitute 13X molecular sieve catalyst indicated it not to be effected by nitrogen oxides but no results were reported on control of nitrogen oxide emissions.

Very little information is in fact available on the reaction between NO and H_2S. Pierce (5-45) studied the gas phase reaction of H_2S with NO and found the reaction to proceed according to equation (5-11). He showed the reaction to be heterogeneous and catalyzed by both silica gel and glass wool. The reaction rate was found to have a negative temperature coefficient over the range of temperature 80 to 212°F, and this was ascribed to the decreased association of NO to N_2O_2 - the reactive specie. Kinumaki and Tominaga (5-46) studied the reaction rates of H_2S and NO in a system catalyzed by small amounts of glass powder. They found that there is no reaction in the absence of moisture, that the reaction had an induction period which depends on the glass powder, and that the reaction rate is controlled by the ratio of the NO to H_2S pressure. Dunnecliff et al. (5-47) studying the reaction in aqueous solution found it to be complex, yielding ammonium thiosulfate, ammonium polysulfide, ammonium nitrite, sulfur, nitrous oxide and nitrogen.

5.4 ADSORPTION OF NO_x BY SOLIDS

A number of solid materials are cited in the literature as adsorbents for oxides of nitrogen. These materials include such common adsorbents as silica gel, alumina, char, and molecular sieves where adsorption is due primarily to physical forces, and metal oxides and hydroxides where the attraction is principally chemical in nature.

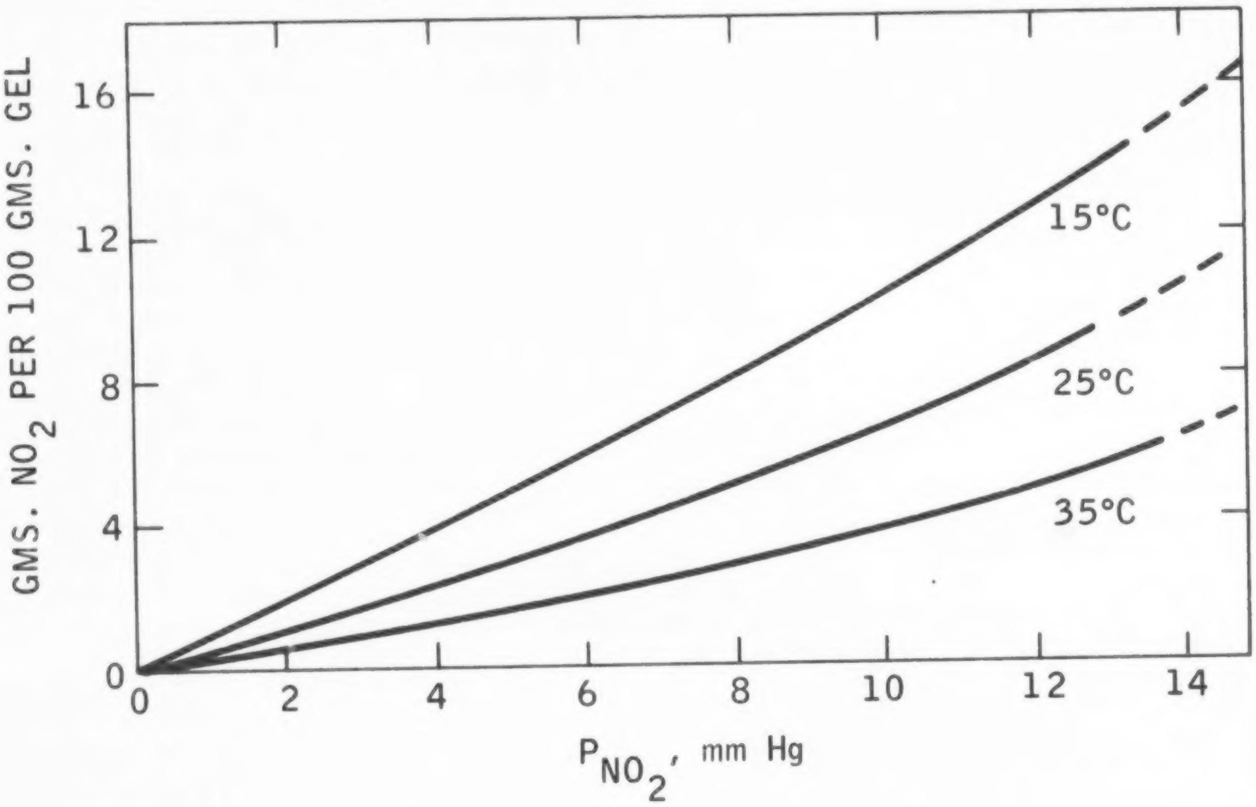
5.4.1 Silica Gel

Silica gel was studied extensively for recovery of the nitric oxide produced by the thermal fixation of nitrogen in the Wisconsin Process. Foster and Daniels, who directed the original work at the University of Wisconsin, reported (5-48) silica gel to have practically no adsorption capacity for NO as such. They also found that while dry silica gel was able to catalyze the oxidation of NO to NO_2 which could then be absorbed, moisture destroyed the catalytic activity. Furthermore, the silica gel was found to have a much higher sorption rate and capacity for moisture than for NO_2.

The capacity of silica gel for NO_2 is not very impressive, even in the absence of moisture. Figure 5-7 shows the adsorption isotherms for the best of seven different silica gels screened by Foster and Daniels. The adsorption capacity can be noted to fall off sharply with increasing temperature.

Figure 5-7

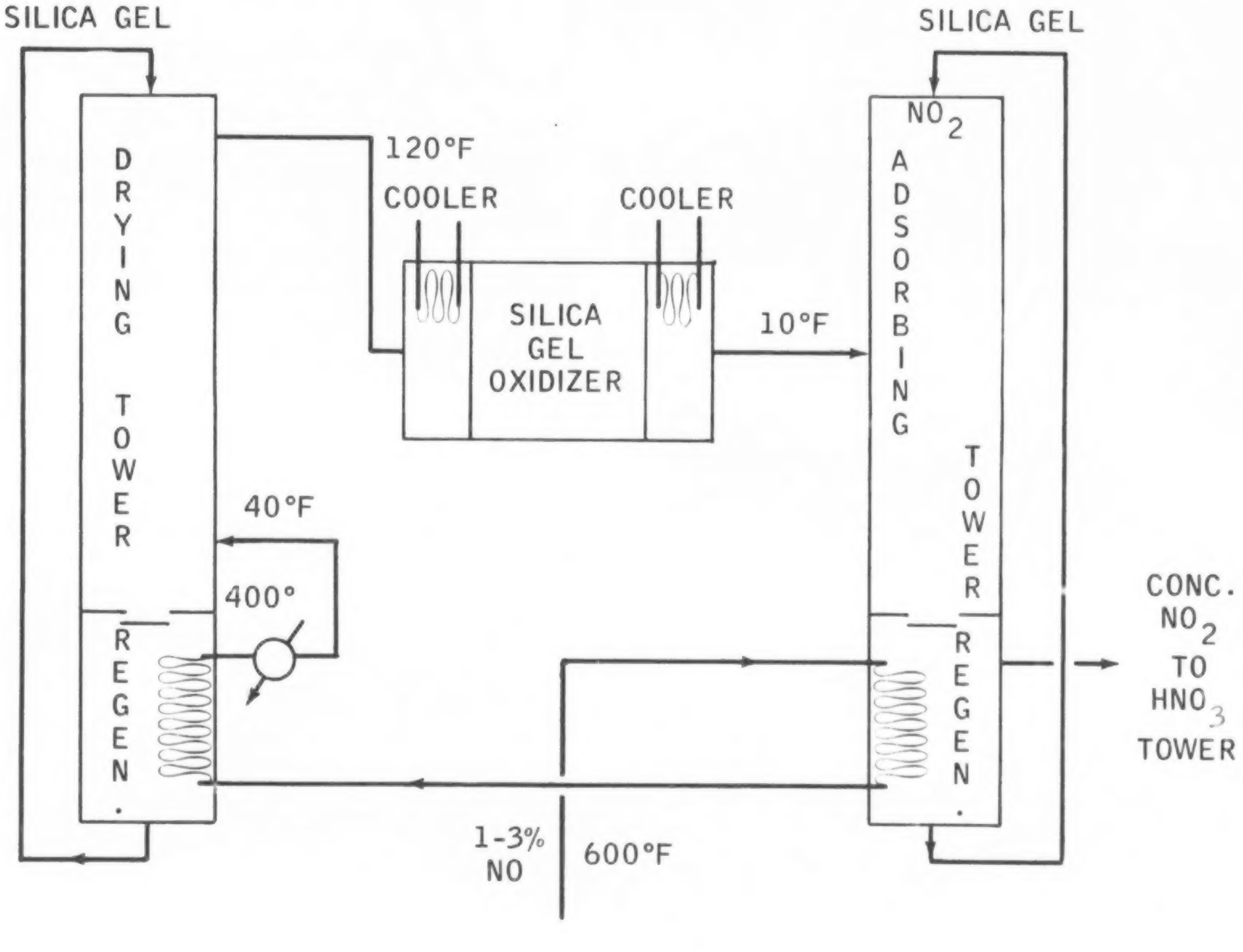
SILICA GEL ADSORPTION CAPACITY FOR NO_2



To achieve reasonable capacity with silica gel, the Wisconsin Process used three fixed beds to dry, oxidize NO, and then adsorb the NO_2 from refrigerated gas. The FMC Company (5-49) who took over the development of the process in 1946 evolved the idea of fluidized beds in place of cycling beds, thus permitting continuous operation. In FMC's version of the process shown in Figure 5-8, the NO-containing gas was dried to a dew point of about -60°F in a fluidized bed of silica gel, oxidized to NO_2 in a second, fixed bed of silica bed, and then cooled to 10°F and adsorbed in another fluidized bed of silica gel. Regeneration of the sorbing gels was carried out by raising their temperature to about 400°F.

Figure 5-8

THE WISCONSIN NITRIC ACID PROCESS


SILICA GEL
SILICA GEL
DRYING TOWER
REGEN.
120°F
COOLER
COOLER
SILICA GEL OXIDIZER
10°F
NO_2
ADSORBING TOWER
REGEN.
40°F
400°
CONC. NO_2 TO HNO_3 TOWER
1-3% NO
600°F

The requirement to dry and cool the gas coupled with the low capacity of silica gel makes this process unattractive for removing dilute NO_x from stack gases. Table 5-13 gives the energy and silica gel requirements reported by Ermenc (5-49) for FMC's process where the NO level in the entering gas is one to two percent. This is three to six times more concentrated with respect to NO than is nitric acid tail gas, and 15 to 30 times more concentrated than is combustion flue gas. Process requirements and investment for such a process could be expected to vary about inversely with the NO concentration.

Table 5-13

Requirements for Wisconsin Process System

	Requirements/Ton of 100% HNO_3 Produced
Power	100 KWH
Water	2700 Gals.
Silica Gel	6 Lbs.
Investment	$50,000

5.4.2. Alumina

Both activated bauxite and alumina were reported by Levenson (5-50) to be better NO_x adsorbents than silica gel but to adsorb water preferentially as does silica gel. On the other hand, Berning, Cristian and Clarke (5-51) found that activated alumina is not as good an adsorbent as silica gel.

Haseba, et al., (5-52) investigated the use of impregnated alumina adsorbents for removal of NO from coke oven gas. Of the 160 kinds of chemicals screened, they found that an adsorbent containing 5% $NaClO_2$ and 10-15% Na_2CO_3 supported on activated alumina worked best. The carbonate acted as a stabilizer for the $NaClO_2$ which by itself was not very effective for removing nitric oxides. With alumina, 100% removal of less than 1 ppm NO was possible until the $NaClO_2$ had been consumed in reaction with NO. Silica gel proved less effective as a carrier. The reaction of NO/NO_2 with the alumina-$NaClO_2$-Na_2CO_3 sorbent is reported (5-53) to be very fast, allowing 100% removal at space velocities as high as 10,000 V/V/Hr and near room temperature. However, the use of alumina, impregnated with $NaClO_2$ or any other consumable oxidant would be impractical for NO_x emission control, since make-up costs for the oxidant would be high.

Although initial laboratory results by Saenz et al (5-54) indicated that a variation of the alkalized alumina process was capable of removing both sulfur dioxide and the oxides of nitrogen from flue gas, later results indicated this not to be the case. The only effect of the alkalized alumina appeared to be to catalyze the decomposition of NO_2 to NO.

5.4.3. Molecular Sieves

The use of molecular sieves for treating nitric acid tail gas is reported by Sundaresan, Harding, May and Hendrickson (5-55). They compared the capacity of silica gel and molecular sieves with a dry gas and obtained the results shown in Figure 5-9. Concentrating on the molecular sieves, they ran a series of cycling experiments using actual nitric acid tail gas in which the nitric oxides concentration ranged from 1800 to 2500 ppm. Results are reported in Table 5-14. Regeneration was accomplished using either a hot air purge, or a combined steam/hot air purge with the nitric oxides being recovered partially as nitric acid and partially as NO_2, as seen in Table 5-15. Neither regeneration techniques appear to have been fully successful in reactivating the sorbent causing a fall-off in capacity with continued cycling.

Figure 5-9

COMPARISON OF NO ADSORPTION CAPACITY FOR MOLECULAR SIEVES AND SILICA GEL

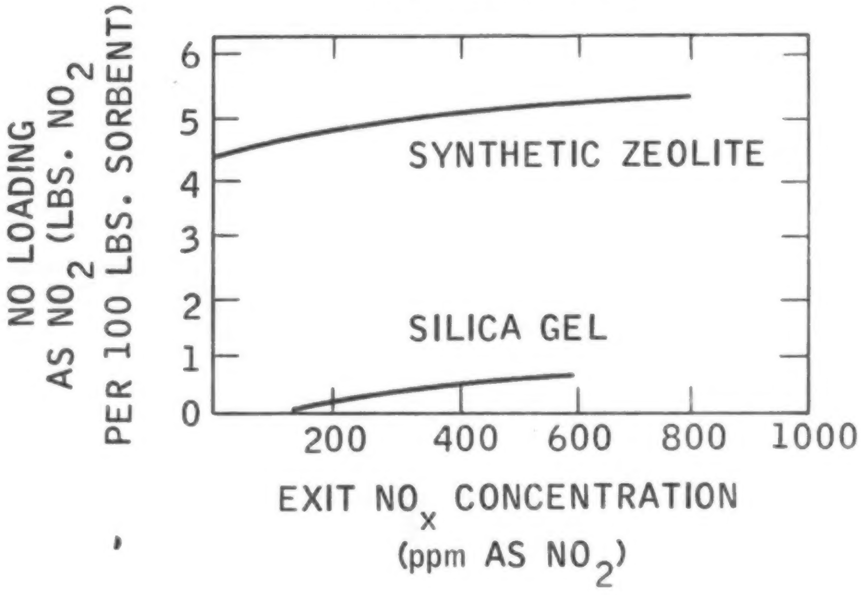


Table 5-14

NO_x Removal in Zeolite Columns

(HNO_3 Plant Tail Gas Feed)

Cycle	Input Gas Temp. °F	Input Gas Psig	Linear Veloc. Ft/Min	Space Veloc. Vol/Hr Vol	Mean Column Temp °F	Exit Concn. at End of Cycle	Lb NO_x Removed 100-Lb Bed: At 200 ppm Exit NO_x	Lb NO_x Removed 100-Lb Bed: End of Cycle	LB H_2O Removed 100-Lb Bed: At 200 ppm Exit NO_x	LB H_2O Removed 100-Lb Bed: End of Cycle
1	82	2.00	20.0	525	92	2400	5.75	6.69	8.26	9.95
2	78	2.00	20.0	525	85	1600	5.00	5.86	6.03	6.98
3	80	2.00	20.0	525	89	3200	3.80	4.44	5.66	7.60
4	84	7.50	51.0	1310	102	800	3.45	4.68	4.26	6.11
5	79	7.50	51.0	1310	94	1050	4.48	5.76	4.45	5.87
6	86	8.00	53.0	1370	102	1000	3.16	5.11	3.72	6.55
7	77	7.00	53.0	1370	95	700	4.96	5.58	5.23	6.16
8	77	2.10	27.0	675	92	300	4.24	4.96	4.39	5.21
9	82	2.80	27.0	675	95	200	4.42	4.42	4.43	4.43
10	94	5.50	48.0	1250	102	800	3.25	4.26	4.27	5.96
11	106	6.20	48.0	1250	109	1500	2.16	3.62	2.72	5.44

Table 5-15

NO_x Recovery from Zeolite Columns

(HNO_3 Plant Tail Gas Feed)

			Recovery of NO_2 in Feed						
			As HNO_3			As NO_2		Total	
Cycle	Total Input G. Moles	Method[(a)]	Acid Strength %	G. Moles	%	G. Moles	%	G. Moles	%
1	3.36	I	25.20	--	--	--	--	--	--
2	2.83	I	27.20	0.20	7.10	2.03	71.80	2.23	78.90
3	2.14	I	36.30	0.69	32.40	--	--	--	--
4	2.26	I	19.30	0.37	16.40	1.20	53.10	1.58	69.29
5	2.78	I	48.20	1.26	45.40	1.22	43.90	2.48	89.30
6	2.46	I	56.50	1.16	47.20	0.93	37.80	2.09	85.00
7	2.69	I	56.40	1.30	48.30	0.79	29.40	2.09	77.70
8	2.42	I	57.60	1.26	52.20	0.95	39.30	2.21	91.50
9	2.40	II	33.40	2.67	--	0.13	--	2.80	--
10	2.05	II	19.40	1.53	74.40	0.13	6.20	1.66	90.60
11	1.75	II	26.80	0.66	--	0.57	--	1.23	--

(a) I = Heat plus air.

II = Heat plus steam plus air.

In a patent based on their work, Sundaresan, et al. (5-56) state that the molecular sieves catalyze the oxidation of NO to NO_2 and the subsequent reaction with water to nitric acid. Data are given in the patent for adsorption of SO_2 as well as NO_x by molecular sieves and also for co-adsorption of SO_x and NO_x. These data are shown in Table 5-16.

Table 5-16

Performance of Synthetic Zeolite Systems

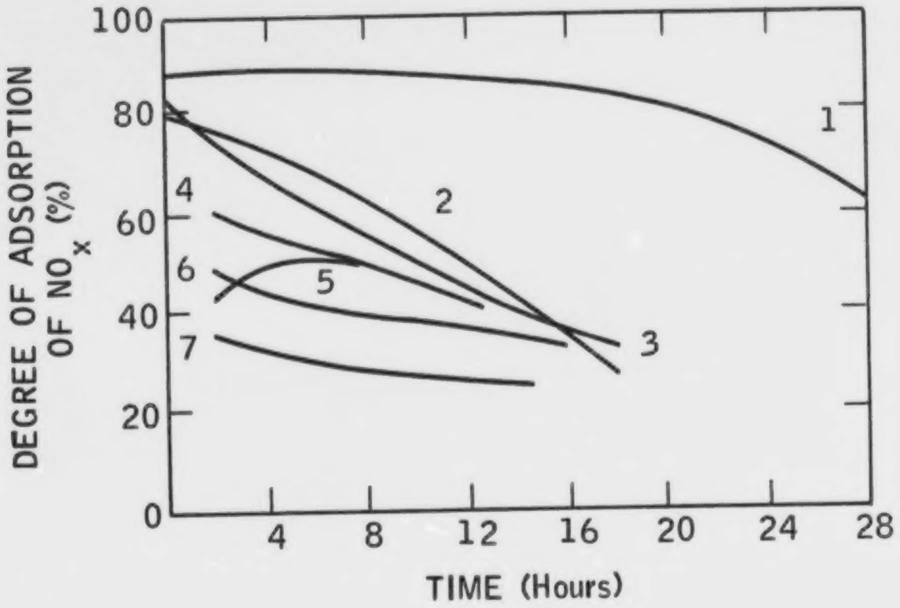
Synthetic Zeolite System, lb.	Volume of Gas Treated, ft^3	Cumulative Volume of Gas ft^3	Gas Concentration in Volume Percent				Loading, lb. of Oxides per 100 lb of Adsorbent	
			NO_x		SO_2			
			In	Out	In	Out	NO_x	SO_2
4.90	- - - -	0.00	0.247	0.000	- - - -	- - - -	- - - -	- - -
	780.00	780.00	0.224	0.000	- - - -	- - - -	4.47	- - -
	140.00	920.00	0.221	0.020	- - - -	- - - -	5.00	- - -
	70.00	990.00	0.218	0.054	- - - -	- - - -	5.50	- - -
	190.00	1,180.00	0.214	0.214	- - - -	- - - -	5.86	- - -
0.69	- - - -	0.00	0.246	0.000	0.121	0.000	- - -	- - -
	40.00	40.00	0.282	0.024	0.121	0.000	1.74	1.15
	80.00	120.00	0.354	0.104	0.121	0.020	5.23	3.26
	136.00	256.00	0.354	0.354	0.120	0.076	8.16	3.87
0.69	- - - -	- - - -	- - - -	- - - -	0.182	0.000	- - -	- - -
	14.00	14.00	- - - -	- - - -	0.248	0.000	- - -	0.74
	16.00	30.00	- - - -	- - - -	0.320	0.020	- - -	1.80
	111.00	141.00	- - - -	- - - -	0.350	0.350	- - -	5.77

5.4.4. Char

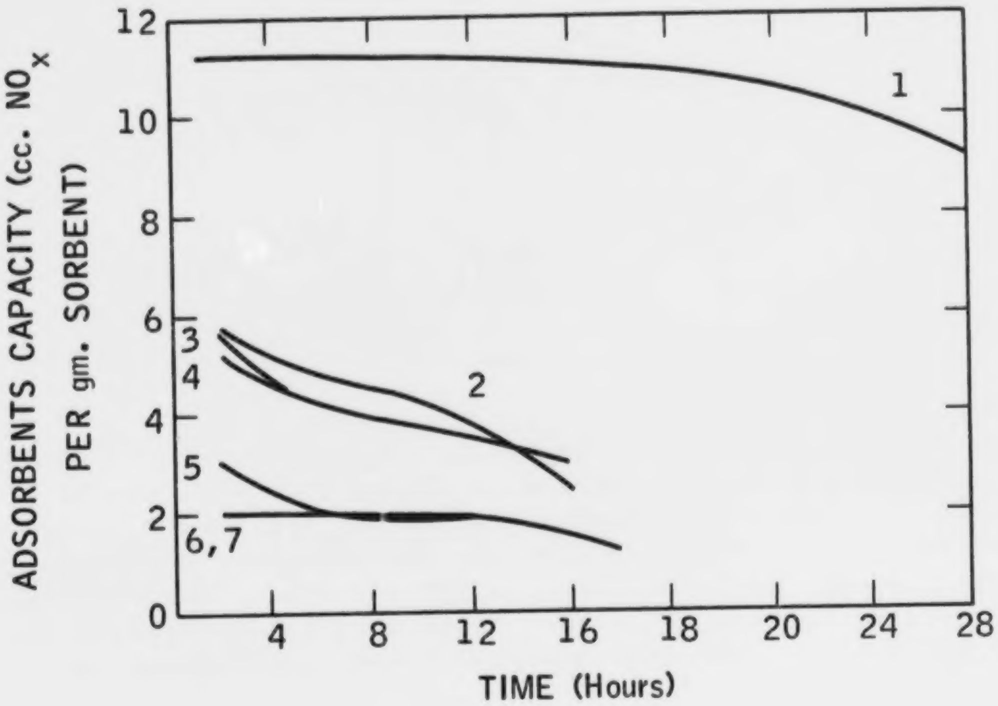
Char is also able to oxidize NO and adsorb it as NO_2. Ganz (5-57), in a study of adsorbents to control NO_x emissions from nitric acid manufacture, found activated carbon to give a higher adsorption rate and capacity than silica gel, aluminum silicates, MnO_2, CuO or Hopcalite. The data of Figure 5.10. were obtained by Ganz with a gas containing .3% NO_x (60% NO, 40% NO_2) at a temperature of about 65°F and a space velocity of 1000 V/V/Hr. Ganz found that complete desorption required temperatures on the order of 400°F to 650°F for the carbon and silica gel. At these temperatures, the carbon ignited and the silica gel crumbled. This led him to conclude that the aluminum silicates were the preferred NO_x adsorbents.

Figure 5-10

CAPACITY OF NO_x ADSORBENTS



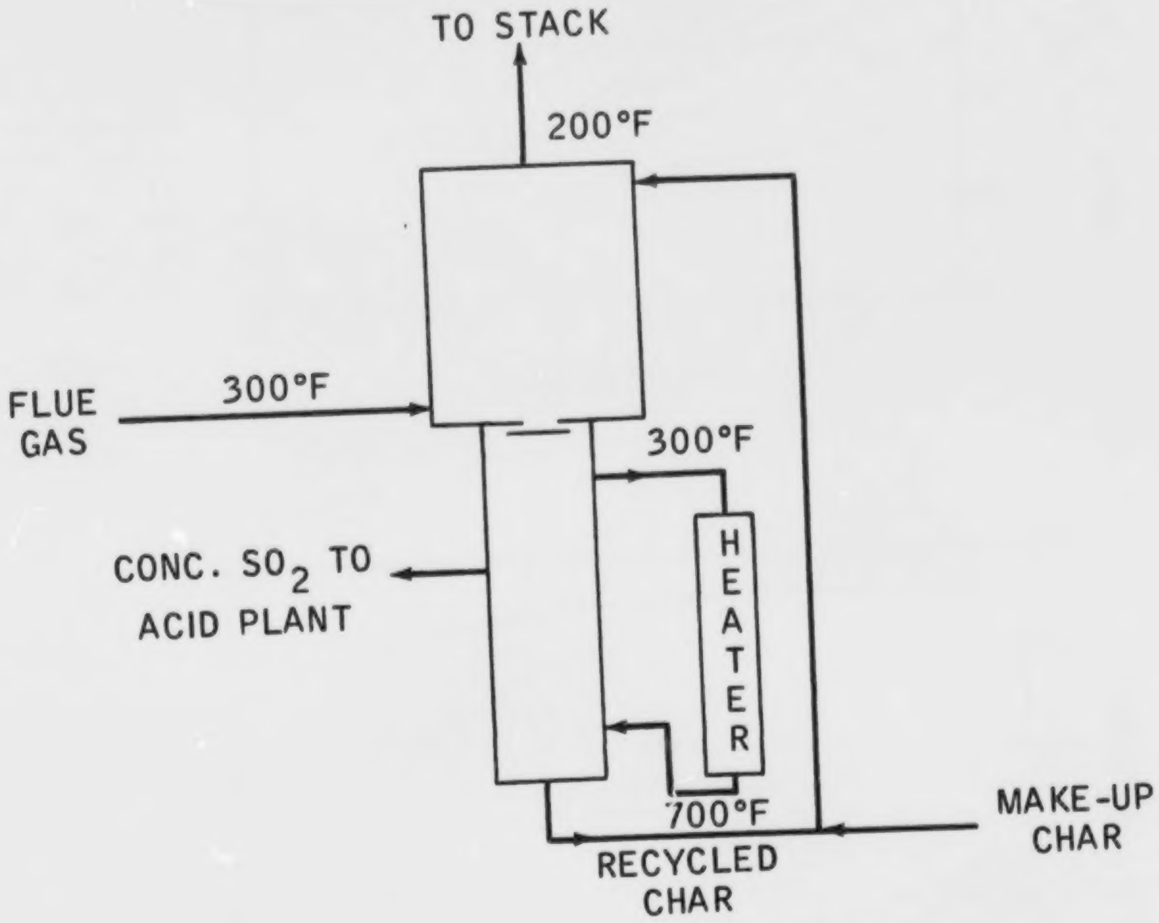
Sorbents: 1) activated carbon, 2) aluminosilicate, 3) silica gel, 4) MnO_2, 5) hopcalite at SV= 1000 $m^3/m^3 \cdot$hour, 6) CuO, 7) hopcalite at SV= 1600 $m^3/m^3 \cdot$hour.



Char is being investigated by the Reinluft Gesellschaft-Essen Germany for the desulfurization of flue gas. The basic outline of their process is shown in Figure 5-11. Others investigating the use of char for flue gas desulfurization are Lurgi in Germany and Hitachi in Japan.

Figure 5-11

REINLUFT SO_2 CONTROL PROCESS



In a patent (5-58) assigned to Reinluft Gesellschaft, the use of charcoal, peat, semi-coke and other char materials is claimed for the removal of both sulfur and nitrogen oxides from stack gases (i.e., as SO_3 and NO_2). According to this patent, the presence of water vapor in the gas increases the capacity of the above sorbents through the formation of H_2SO_4 and HNO_3. Adsorbed oxides are said to be recovered by heating the carbonaceous material to temperatures ranging between 600 and 1100°F, where the adsorbed oxides are reduced and

Adsorbed		Desorbed	
$2SO_3 + C$	$\longrightarrow$	$2SO_2 + CO_2$	(5-12)
$2NO_2 + C$	$\longrightarrow$	$2NO + CO_2$	(5-13)

desorbed. No capacity data for NO are given. Haagen-Smit (5-59) however found the breakthrough capacity of char for nitric oxides to be about 5% that of SO_2 with powerplant flue gas. The Reinluft process designed for SO_2 control is already very expensive (5-60) and a similar process for NO_x alone or for both NO_x and SO_2 would be even more so. Furthermore, the use of chars as adsorbents for NO_x removal constitute a potential fire or explosion hazard.

5.4.5. Ion Exchange Resins

In tests made at the U.S. Volunteer Ordnance Works (5-51), ion-exchange resins were found to be more effective than other adsorbents for the removal of nitrogen oxides released in the production of nitric acid. With moisture-free gases, silica gel, activated carbon, and ion exchange resins Amberlite IRA-401 and Dowex 1-XI proved best for adsorption of nitrogen oxides. Activated alumina, Floridin B, Florex B, Mobilbead, and ion exchange resin Amberlite IRC-50 showed slight adsorption capacities while molecular sieves, Unicrest, Florisil, Floridex B, Celkate, white vermiculite, Amberlite IR-120 and IR-4B showed no nitrogen oxides adsorption capacity. Since the carbon and silica gel were found to preferentially adsorb water to the exclusion of nitrogen oxides, they were excluded from further consideration. Tests also showed that NO alone was not appreciably adsorbed by Amberlite IRA-401 or Dowex 1-X1, the two best resins.

5.4.6. Metal Oxides and Sulfides

The higher oxides of nitrogen (e.g., N_2O_3, NO_2, etc.) can combine with most of the less refractory metal oxides to form nitrates and nitrites. Metal superoxides undergo similar reaction with NO. Although the lower metal oxides and hydroxides are incapable of undergoing simple addition reactions with NO, more complex reactions are possible. Barnes (5-61) showed that alkaline hydroxides react with nitric oxides to form nitrites, nitrogen, and nitrous oxide.

$$4NO + 2MOH \longrightarrow N_2O + 2MNO_2 + H_2O \qquad (5\text{-}14)$$

$$6NO + 4MOH \longrightarrow N_2 + 4MNO_2 + 2H_2O \qquad (5\text{-}15)$$

(M = Li, Na, K, Rb, Cs, Ca, Sr, and Ba)

Using pure NO, Barnes found that the rates of these reactions increased with the atomic weight of the element. At room temperature, for example, he found that the complete reaction required several years with LiOH, several months with NaOH, several days with KOH and several hours with RbOH and CsOH. CsOH appeared to be the most reactive, yielding the results shown in Table 5-17.

Table 5-17

Reaction of CsOH with NO

Contact Period	Temp., °C	Composition of Resulting Gas, Mole % (Dry Basis) N_2O	N_2
40 sec.	260	33	67
1 min.	290	29	71
10 min.	290	27	73
30 min.	290	21	79

Some metal oxides are able to catalyze the oxidation of NO by oxygen and are then able to react with it. Manganese dioxide and cobalt oxide are examples of such oxides. The Food Machinery and Chemical Corp. (FMC) working under contract to the Air Force (5-62) studied these oxides for adsorbing and concentrating the NO product from the thermal fixation of air. Manganese dioxide was found to lose one third of its activity in two weeks of laboratory use with adsorption conditions of 2% NO in air at 570°F. Cobalt oxide lost activity at almost twice this rate. Other unsuccessful sorbents tested by FMC are shown in Table 5-18.

FMC did find one adsorbent-alkalized ferric oxide (sodium ferrate) which offered some promise for concentrating nitric oxide. The elementary reaction involved in the use of the alkalized ferric oxide is shown below:

$$2NO + 3/2\ O_2 + Na_2Fe_2O_4 \underset{1400°F}{\overset{750°F}{\rightleftarrows}} 2\ NaNO_3 + Fe_2O_3 \qquad (5\text{-}16)$$

Pilot plant experience was generally encouraging with this system and concentrations of about 40% were produced in desorption. The major problem found was that both the adsorber and regenerator were operated as fluidized beds and as the sodium nitrate content in the sorbent increased the sorbent particles would agglomerate to a size that could not be easily fluidized. At sorption and desorption temperatures, sodium nitrate is molten and was the agent responsible for agglomeration. A further problem was caused by decomposition of some of the nitric oxide during regeneration.

Table 5-18

Activity of Various Sorbents - Evaluated by FMC

Sorbent	Activity
$CuWO_4$	No activity 200° to 400°C
$Fe_2(WO_4)_3$	No activity 170° to 475°C
$CoWO_4$	No activity 200° to 480°C
$Cu(VO_3)_2$	No activity 200° to 450°C
$Fe(VO_3)_3$	No activity 200° to 450°C
$PbCrO_4$	No activity 140° to 430°C
$CoMoO_4$	No activity 190° to 490°C
$PbMoO_4$	No activity 160° to 430°C
$2CuO \cdot CuCrO_4$	Very poor activity 375° to 400°C probably due to CuO
NiO	Very poor activity at 500°C
$AgCrO_4$	Very poor activity at 400°C Material apparently reduced
$NiWO_4$	Very poor activity at 400°C
$BaMnO_4$	Very poor activity at 330°C Material not stable
Ag	Very poor activity at 390°C
$NiCrO_4$	Poor activity at 375°C. Material deactivated or decomposed
B_2O_3	Poor activity 450° to 490°C
Fe_2O_3	Moderate activity 240° to 370°C Deactivated rapidly
CrO_2	Moderate activity 325°C Deactivated or decomposed
$CuMoO_4$	No activity 200° to 500°C
$Ag_2M_2O_4$	No activity 140° to 410°C
SnO_2	No activity 200° to 480°C
CdO	No activity 190° to 430°C
ZnO	No activity 190° to 480°C
WO_3	No activity 220° to 440°C
CuO	Moderate activity 350° to 390°C Deactivated rapidly
Co_2O_3	Good activity at 300°C but deactivated rapidly
MnO_2	Good activity at 300°C but deactivated rapidly
$CuMnO_3$	Good activity at 300°C but deactivated rapidly

Jordan, Ward, and Fulweiler (5-63) studied the adsorption of NO by more than 300 metal sulfides for purifying coke oven gas. Using pure nitric oxide, they obtained the results shown in Table 5-19 for sulfides with and without alkali. Alkalized iron sulfides gave the best results, forming compounds similar to the Roussin complex salts $KFe_4(NO)_7S_3$. Such complexes are unstable in oxidizing atmospheres and at all but low temperatures. Therefore, the use of these adsorbents is of doubtful value for control of flue gas NO emissions.

Table 5-19

Adsorption* of NO By Metal Sulfides With and Without Alkali

Sulfide	Adsorption of Dry Substance or Mixture, Per Cent by Weight	
	Without Alkali	With 50% Alkali
Iron	--	20.6 ($CaCO_2$)
Iron	--	32.9 (Na_2CO_3)
Iron	10.9	27.1 ($NaHCO_2$)
Iron (ferrous)	13.4	11.3
Cobalt (ous)	6.8	17.9
Nickel (ous)	19.2	6.7
Manganese (ous)	0.51	2.4
Tungsten (sulfided tungstic anhydride)	0.33	3.2
Molybdenum (sulfided molybdenum sesquioxide)	1.7	1.4
Molybdenum (sulfided molybdic acid)	0.28	5.5
Arsenic (ous)	Nil	0.05
Arsenic (di-)	0.13	0.16
Antimony (ous, red)	0.25	3.6
Antimony (ous, black)	0.12	0.02
Antimony (penta-)	0.23	0.93
Bismuth	0.77	1.6
Tin (ous, hydrosulfide)	1.0	1.5
Tin (ous)	0.52	2.0
Tin (ic)	2.4	1.9
Lead	0.34	0.87
Aluminum	Nil	--
Magnesium	0.53	--
Strontium	4.3	--
Barium	5.6	2.6 (Na_2CO_3)
Calcium	3.2	--
Mercury (ous)	0.09	1.7
Mercury (ic)	0.15	1.5
Cadmium	0.53	3.3
Zinc	0.39	1.7
Silver	0.38	1.5
Copper (ous)	0.51	2.5
Copper (ic)	0.48	3.3
Sodium (di-, sulfided Na_2CO_3)	0.49	--
Sodium (hydro-, sulfided moist Na_2CO_3)	2.2	--

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* Pure NO passed through tube containing adsorbent at ambient temperatures for five hours.

5.5 ABSORPTION OF NITROGEN OXIDES

Absorption is the removal of a gas by a liquid as a result of its reaction with or its solubility in that liquid. Nitrogen oxides are absorbed by a large number of liquids.

Table 5-20

Nitrogen Oxides Absorbents

- Water

  $H_2O + NO \longrightarrow$ No Reaction

  $H_2O + N_2O_3\ (NO + NO_2) \longrightarrow 2HNO_2$

  $H_2O + 3NO_2 \longrightarrow 2HNO_3 + NO$

- Hydroxide and Carbonate Solutions

  $2MOH + NO \longrightarrow$ No Reaction

  $2MOH + N_2O_3\ (NO + NO_2) \longrightarrow 2MNO_2 + H_2O$

  $2MOH + 2NO_2 \longrightarrow MNO_2 + MNO_3 + H_2O$

  $M_2CO_3 + NO \longrightarrow$ No Reaction

  $M_2CO_3 + N_2O_3\ (NO + NO_2) \longrightarrow 2MNO_2 + CO_2$

  $M_2CO_3 + 2NO_2 \longrightarrow MNO_2 + MNO_3 + CO_2$

  $M = Na^+, K^+, NH_4^+, Ca^{++}$, etc.

- Molten Alkali Carbonates or Hydroxides

  $M_2CO_3 + 2NO_2 \longrightarrow MNO_2 + MNO_3 + CO_2$

- Sulfuric Acid

  $H_2SO_4 + NO \longrightarrow H_2SO_4 \cdot NO$

  $2H_2SO_4 + N_2O_3\ (NO + NO_2) \longrightarrow 2NOHSO_4 + H_2O$

- Solutions of Complex Forming Salts
- Organic Solutions

5.5.1. Aqueous Alkaline Solutions

Nitric oxide does not itself combine with water or basic solutions. Absorption in these cases requires that at least part of the NO be oxidized to NO_2, and complete removal requires that half of it be so oxidized. More complete oxidation is not needed, and may in fact be undesirable. Sherwood and Pigford (5-64) citing data of Eagleton, Langer and Pigford showed that at a 1% concentration of total nitrogen oxides in the gas, a 46% NaOH solution absorbed nitrogen oxides from a gas containing equal molar quantities of NO and NO_2 as much as ten times faster than NO_2 alone. When they compared the NO + NO_2 absorption rates with the calculated equilibrium concentrations of N_2O_3 ($NO + NO_2 \rightarrow N_2O_3$), they found that the rate was approximately proportional to the first power of the N_2O_3 concentration indicating it to be the reacting specie. Ganz and coworkers (5-65,66,67) studying the absorption of nitrogen oxides by solutions of $Ca(OH)_2$ and Na_2CO_3 also found that equal molar mixtures of NO and NO_2 were as easily or more easily absorbed than NO_2 alone. Mirev et al. (5-68) found that the completeness of the reaction between a NaOH solution and NO/NO_2 mixtures reached a maximum at a 1:1 molar mixture of these oxide.

The work of Atroshchenko (5-69) helps explain the result of the few researchers who have found NO_2 to be more readily absorbed than NO + NO_2. Atroschenko studied the absorption of equal concentrations of NO_2 and NO + NO_2 over H_2O and NaOH solution by three methods: a static method where there was no relative movement between the gas and the absorbents, a bubbling method in which the gas was bubbled through the liquids, and a countercurrent flow method where the gas was moved countercurrent to a falling film of absorbent. With the static method, the rate of absorption for NO_2 was found to be greater than for NO + NO_2 whereas for the other two methods the reverse was true.

Koval and Peters (5-70) studying the effect of NO addition on the reaction of NO_2 with water found that the NO is absorbed along with the NO_2 to form nitrous acid and that the removal rate of nitrogen dioxide is only slightly changed by the addition. They developed two rate equations to account for the behavior observed:

$$\frac{-dNO_2}{dt} = k_1 (NO_2)^2 + k_2 (NO)(NO_2) - k_3 (HNO_2)^2 \qquad (5\text{-}17)$$

$$\frac{-d(NO)}{dt} = k_2' (NO)(NO_2) - k_3' (HNO_2)^2 \qquad (5\text{-}18)$$

where: k_1, k_2, k_2', k_3 and k_3' are rate constants.

An examination of the second equation shows that the absorption of NO will not take place when there is no NO_2 present and that in a basic solution (i.e., HNO_2 is zero), the rate of disappearance of NO will be a maximum when half the NO is oxidized to NO_2 and that when less than half the nitrogen oxides are present as the higher oxide, absorption provides less than complete nitrogen oxides removal.

Chambers and Sherwood (5-71), in apparent contradiction to the above equations, found that NaOH solutions showed lower rates of absorption for NO_2 than did pure water. Atroshchenko also found the rate of absorption to increase with dilution. Perelman and Kantoravich (5-72) explained these results by considering the absorption of $NO + NO_2$ to take place by a number of steps beginning with their association to N_2O_3, diffusion of N_2O_3 into the liquid film, reaction with H_2O to form HNO_2, and finally neutralization of acid by the alkali if present. They concluded that diffusion through the liquid film was the rate controlling step and that the lower the solution density (concentration) the faster this diffusion would be. From this standpoint, H_2O would be the best absorbent at low utilizations where there exists no need to neutralize the HNO_2 formed to prevent its buildup and dissociation. Soluble nitrites formed by this neutralization were also found to decrease the rate of absorption in the same manner while the content of insoluble free alkali had no effect except that below a certain level, absorption underwent a sharp decrease. The study of Perelman and Kantoravich also showed the rate of absorption to be independent of gas velocity indicating gas film diffusion to be unimportant in the absorption process.

Some data on actual control of plant nitrogen oxide emissions by aqueous scrubbing is reported by Streight (5-73) and by Krastev and Georgieva (5-74). Streight reports on an actual control system built by Dupont to remove nitrogen oxides from the effluent gases of a nitric acid and nylon intermediates plant. Although a caustic soda liquor proved satisfactory in this system, it was found that the operating costs could be substantially reduced by using an available water-ammonia-caustic soda solution (0.5% NaOH, 45% Na_2CO_3, and 0.03-0.5% NH_3). Krastev and Georgieva conducted their tests by installing an Na_2CO_3 packed tower absorber on one of the operating nitric acid absorbing towers at the Diemetrovgrad Chemical Combine (Russia). The results obtained paralleled those of Perelman and Kantoravich as to the effects of $NaNO_2$ and $NaNO_3$ and Na_2CO_3 in the scrubbing solution.

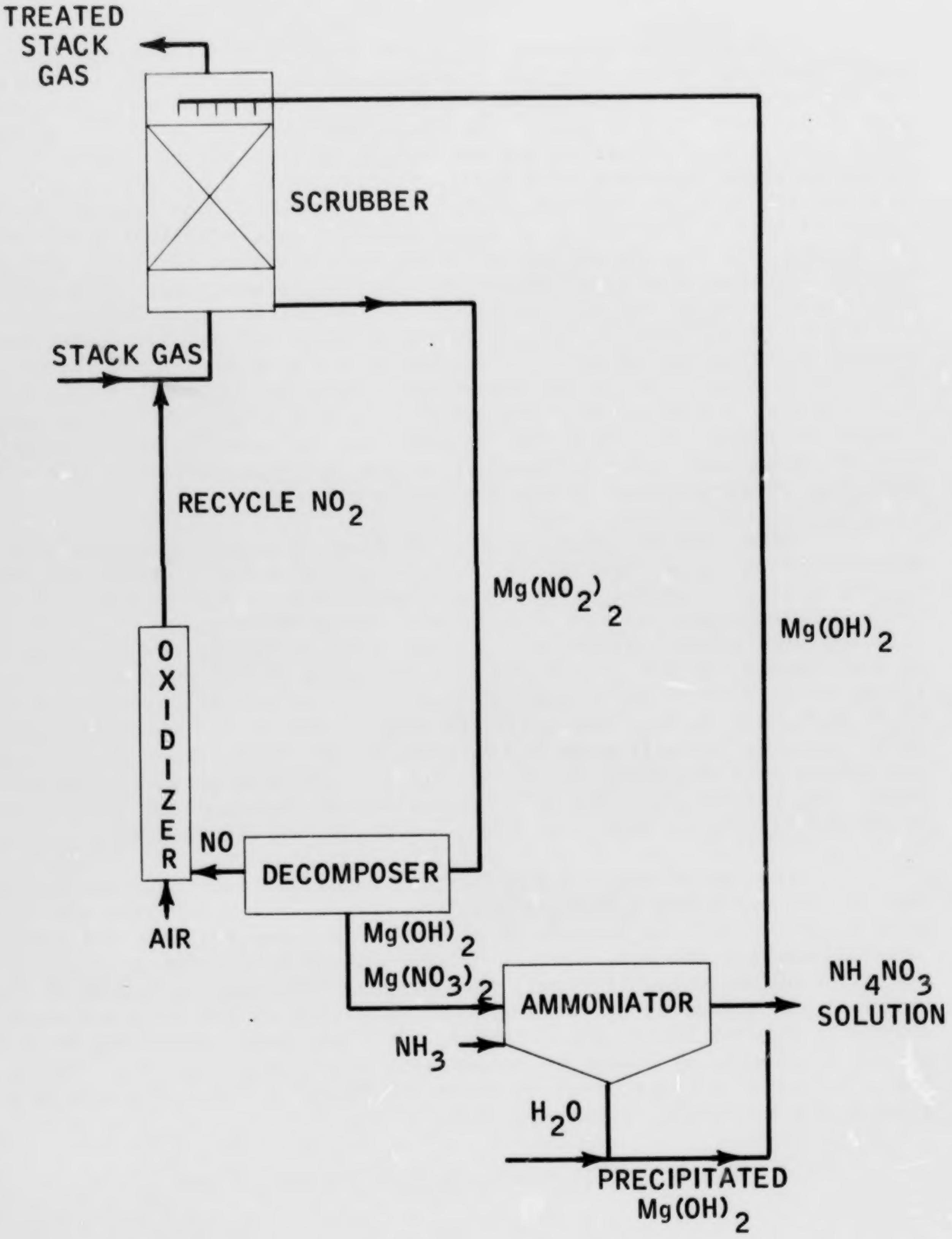
The use of magnesium hydroxide, magnesium carbonate and mixtures of the two for scrubbing nitric oxides from nitric acid plant vent gas is described in a patent by Schmidt et al (5-75). Recognizing that optimum removal necessitates that the N_2O_3 content of the mixture be as high as possible (i.e., equimolar NO/NO_2 concentration), they propose recycling either NO or NO_2 to the vent gas depending on the degree of oxidation of the nitrogen oxide initially present in the gas. Recycle NO is obtained, according to the claims of the inventors, by thermally decomposing the $Mg(NO_2)_2$ solution formed in the scrubber at a temperature of about 300 to 400°F and a pressure of 4 to 7 atmospheres according to the equation:

$$3Mg(NO_2)_2 + 2H_2O \rightarrow Mg(NO_3)_2 + 2Mg(OH)_2 + 4NO \quad (5\text{-}19)$$

The resulting suspension of magnesium hydroxide in the magnesium nitrate liquor can be treated with NH_3 or mixtures of NH_3 and CO_2 to yield additional precipitated magnesium hydroxide or magnesium hydroxide and carbonate and a solution containing NH_4NO_3. Figure 5-12 shows a flow diagram of the basic process described by the invention.

Figure 5-12

$Mg(OH)_2$ SCRUBBING PROCESS


TREATED STACK GAS
SCRUBBER
STACK GAS
RECYCLE NO_2
$Mg(NO_2)_2$
$Mg(OH)_2$
OXIDIZER
NO
DECOMPOSER
AIR
$Mg(OH)_2$
$Mg(NO_3)_2$
AMMONIATOR
NH_4NO_3 SOLUTION
NH_3
H_2O
PRECIPITATED $Mg(OH)_2$

If it is desirable to recycle NO_2 instead of NO (as it would be if most of the nitrogen oxides in the vent gas were present as NO), the off gas from the decomposer is first oxidized with air or oxygen as shown above before being introduced into the vent gas.

The potential of using an alkaline scrubbing process for control of power plant nitrogen oxide emission is borne out by separate test data obtained by Combustion Engineering (5-76) and Universal Oil Products (5-77). Both report 20% nitrogen oxides removal in their caustic scrubbing desulfurization processes. Such removal suggests that about 10% of the NO present in flue gas is oxidized to NO_2 as the flue gas cools just before or in the scrubber, and that this NO_2 combines with an equal amount of NO to react with the caustic solution as N_2O_3.

5.5.2. Molten Alkali Metal Carbonates

North American Rockwell (Atomic International Division) working under contract to NAPCA (PH 86-67-128) has investigated the extension of its molten carbonate flue gas desulfurization technique to control of NO_x emissions. Their test data (5-78) show that over 50% of the NO can be removed in a molten carbonate reactor when CO_2 is absent from the gas. With CO_2 present, however, removal efficiencies are low (i.e., $<$ 15%). Furthermore with only 4% each of sodium nitrate and sodium nitrite, expected reaction products of the melt with NO and O_2, the removal efficiency even in the absence of CO_2 gas was only 12%. The nitrites and nitrates in the melt are believed to drive the NO removal reaction shown below to the left:

$$2NO + O_2 + M_2CO_3 \rightleftharpoons MNO_2 + MNO_3 + CO_2 \quad (5\text{-}20)$$

The addition of CO_2 in this case resulted in a total nitrogen oxide concentration in the reactor effluent that was 25% higher than in the inlet gas stream.

5.5.3. Sulfuric Acid

The ability of strong sulfuric acid solution to absorb nitric oxides has long been recognized and is an integral step of the Lead Chamber Process for producing sulfuric acid (5-79). Two nitrogen oxide-sulfuric acid compounds are formed in this process - violet acid $H_2SO_4 \cdot NO$, and nitrosyl sulfuric acid $NOHSO_4$. In the former, the NO is only loosely bound to the sulfuric acid. Nitrosyl sulfuric acid is very stable in concentrated acid but becomes less so with increasing dilution. The nitrosyl sulfuric acid is formed by reacting equal molar quantities of NO and NO_2 with acid:

$$NO + NO_2 + 2H_2SO_4 \rightleftharpoons 2NOHSO_4 + H_2O \quad (5\text{-}21)$$

Since sulfuric acid is such an effective dehydrating agent, moisture present in the gas that is scrubbed remains with the acid and promotes the reverse reaction. H_2SO_4 also forms a complex with NO_2 alone. Ganz (5-80) in a study of the kinetics of the absorption of nitrogen oxides by sulfuric acid, however, found that as with alkaline scrubbing, the rate of absorption of equal molar mixtures of NO and NO_2 in sulfuric acid is faster than the rate of absorption of NO_2 alone, especially under turbulent absorbing conditions. Ganz also found that increasing the temperature lowered the absorption rate. His experimental results are shown in Figure 5-13. This decrease in rate can be explained by the decrease in association of NO + NO_2 to N_2O_3 with increasing temperature. Figure 5-14 shows Ganz's data on the effects of acid and nitrogen oxide concentration on the absorption rates. Similar effects of temperature and concentration are reported by Safiullin et al (5-81) and by Stopperka et al (5-82).

Figure 5-13

DEGREE OF ABSORPTION OF N_2O_3 AS A FUNCTION OF THE TEMPERATURE IN 92% H_2SO_4 AT A SPACE VELOCITY OF 500 V/V/HR.

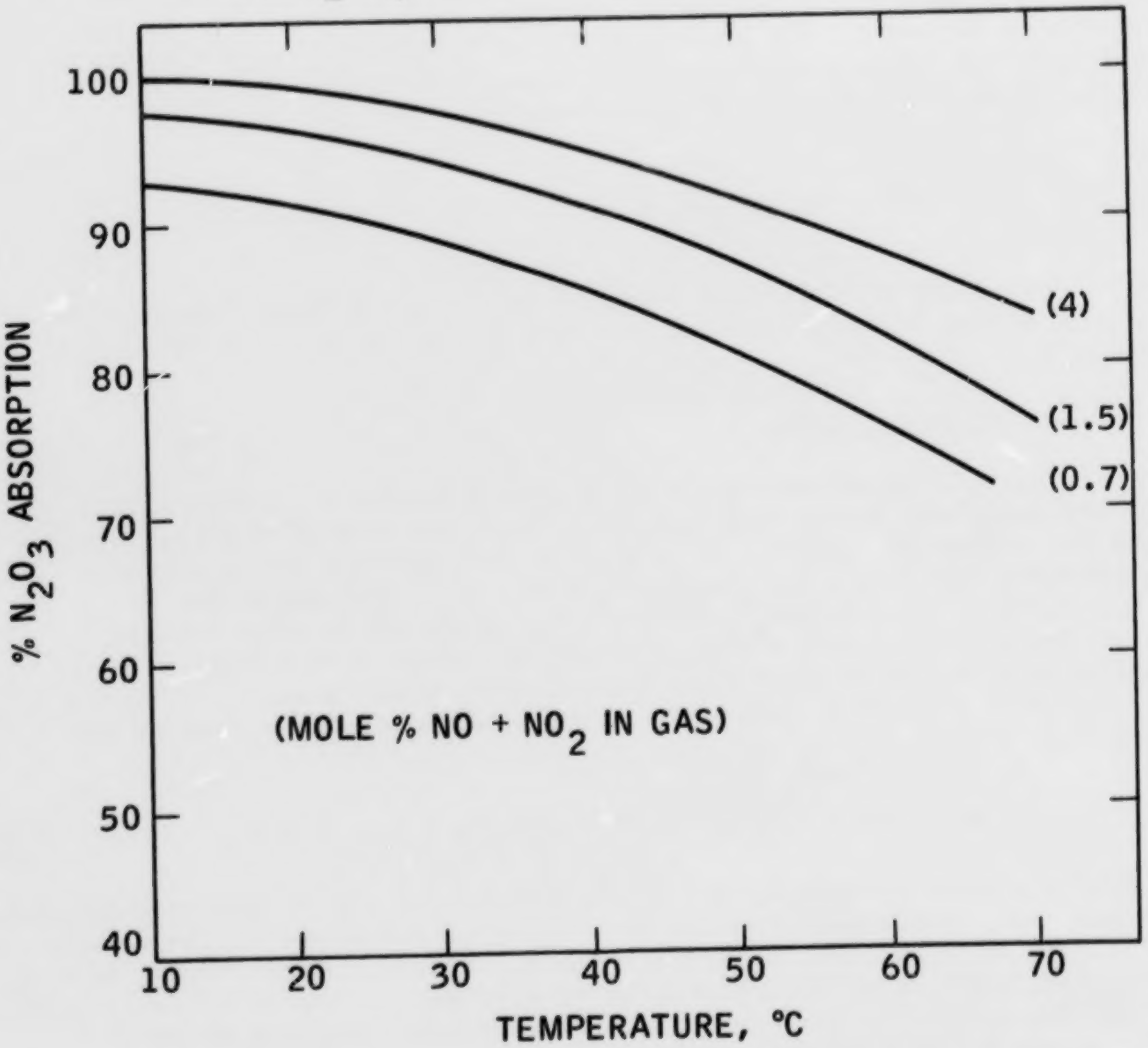
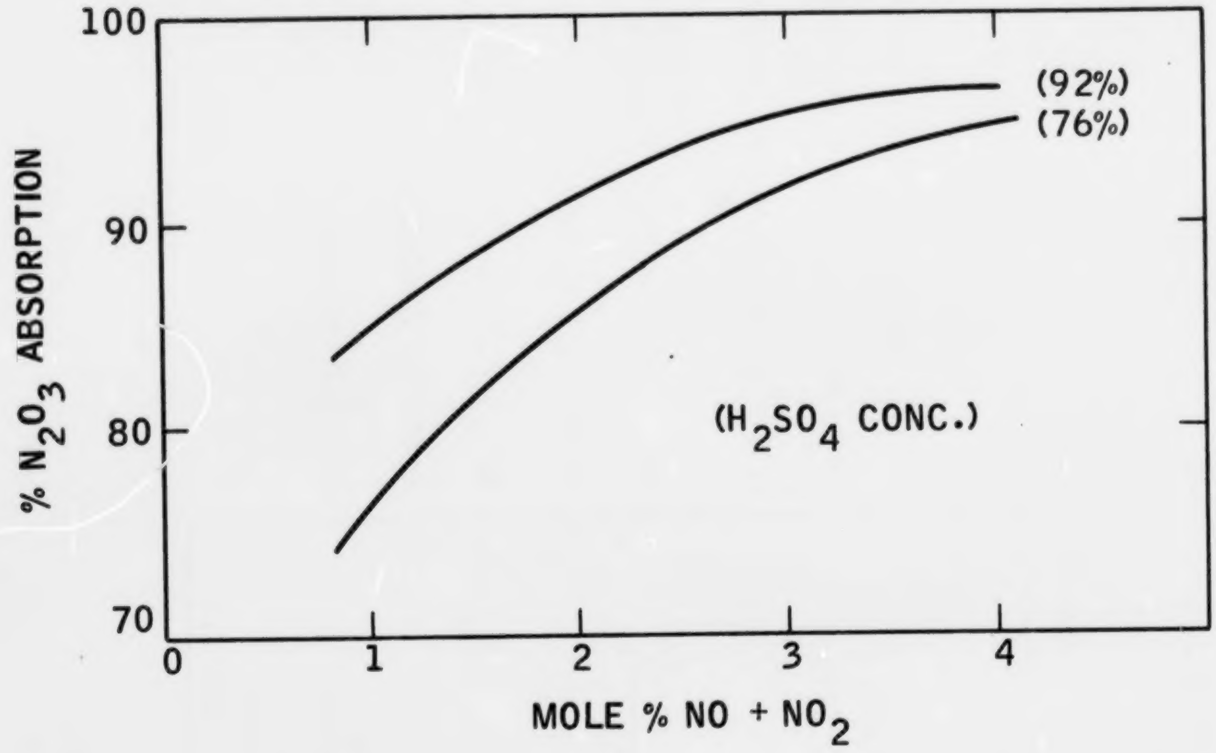


Figure 5-14

DEGREE OF ABSORPTION AS A FUNCTION OF THE CONCENTRATION OF NO + NO_2 IN THE GAS AND SULFURIC ACID AT A SPACE VELOCITY OF 700 V/V/HR.

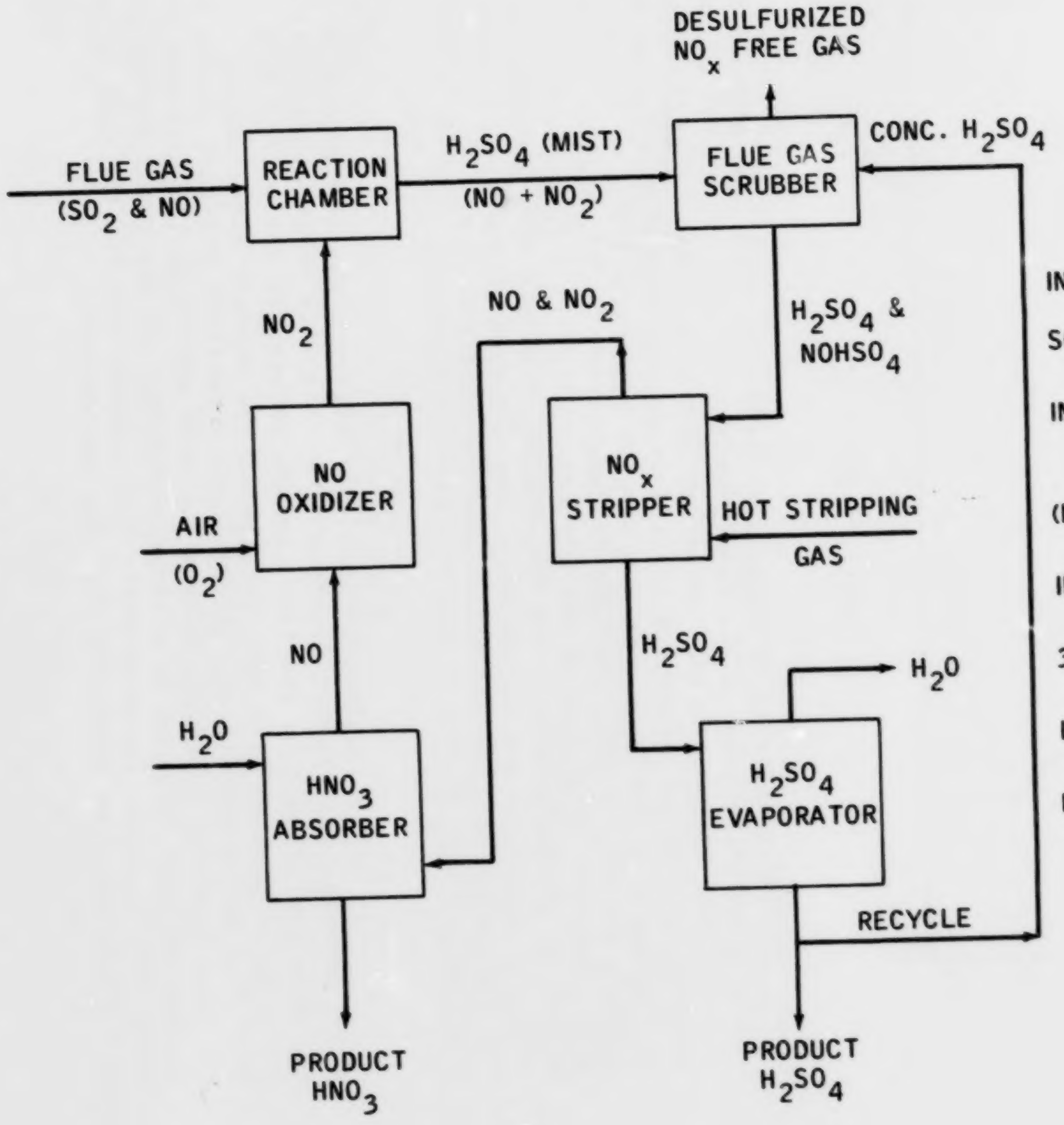


Under contract to NAPCA (PH-86-69-75), Tyco Laboratories is studying modifications of the Lead Chamber Process for control of both nitrogen and sulfuric oxides emissions from power plants (5-82). Flow diagrams of the two alternate control processes they have proposed are shown in Figures 5-15 and 5-16. To achieve the optimum 1:1 NO_2 to NO ratio and to oxidize the SO_2 to SO_3, the Tyco Processes recycle NO_2 back to the flue gas. Complete oxidation of the SO_2 takes place in a few seconds at temperatures of about 300°F. The SO_3 and NO_2 + NO are then absorbed in 80% sulfuric acid. In a separate step, the nitrogen oxides are stripped from the acid. The stripped nitric oxides are oxidized to NO_2 for recycle to the flue gas and to nitric acid for sale as a product.

In their original process, the absorber was operated with 80% H_2SO_4 entering the chamber at about 80°F. At this temperature, most of the moisture present in the flue gas was removed by the acid. This was a major problem with this version of the process since combustion flue gases contain relatively large amounts of moisture (Table 5-1). The heat required to reconcentrate the acid and strip the nitrogen oxides in this process amounted to a large percentage of the total boiler heat rate. For a boiler fired by coal, fuel consumption for the control process alone would be about 40% that for the boiler.

FIGURE 5-15

TYCO'S ORIGINAL SULFURIC ACID SCRUBBING PROCESS


DESULFURIZED
NO_x FREE GAS
FLUE GAS
(SO_2 & NO)
REACTION CHAMBER
H_2SO_4 (MIST)
(NO + NO_2)
FLUE GAS SCRUBBER
CONC. H_2SO_4
NO_2
NO & NO_2
H_2SO_4 &
$NOHSO_4$
NO OXIDIZER
AIR
(O_2)
NO_x STRIPPER
HOT STRIPPING
GAS
NO
H_2SO_4
H_2O
H_2O
HNO_3 ABSORBER
H_2SO_4 EVAPORATOR
RECYCLE
PRODUCT
HNO_3
PRODUCT
H_2SO_4

IN THE FLUE GAS REACTION CHAMBER:

$SO_2 + NO_2 + H_2O \longrightarrow H_2SO_4 \text{ (MIST)} + NO$

IN THE SCRUBBER AND NO_x STRIPPER:

$(NO_2 + NO) + 2H_2SO_4 \underset{\text{STRIPPER}}{\overset{\text{SCRUBBER}}{\rightleftarrows}} 2NOHSO_4 + H_2O$

IN THE HNO_3 ABSORBER:

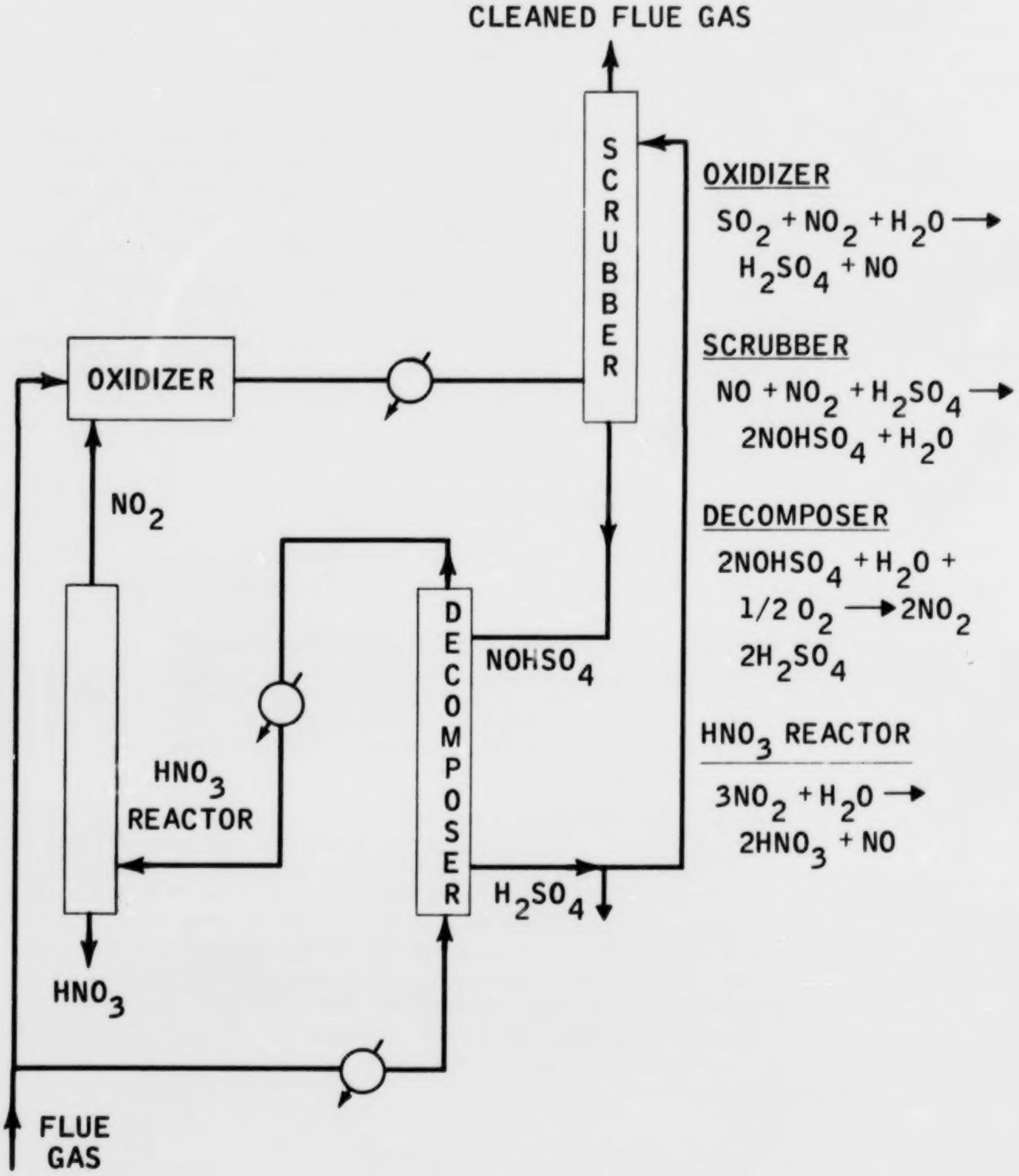
$3NO_2 + H_2O \longrightarrow 2HNO_3 + NO$

IN THE NO OXIDIZER:

$NO + \frac{1}{2}O_2 \longrightarrow NO_2$

Figure 5-16

TYCO'S MODIFIED SULFURIC ACID SCRUBBING PROCESS


CLEANED FLUE GAS
SCRUBBER
OXIDIZER
NO_2
DECOMPOSER
$NOHSO_4$
HNO_3 REACTOR
H_2SO_4
HNO_3
FLUE GAS
OXIDIZER
$SO_2 + NO_2 + H_2O \rightarrow H_2SO_4 + NO$
SCRUBBER
$NO + NO_2 + H_2SO_4 \rightarrow 2NOHSO_4 + H_2O$
DECOMPOSER
$2NOHSO_4 + H_2O + 1/2\ O_2 \rightarrow 2NO_2\ 2H_2SO_4$
HNO_3 REACTOR
$3NO_2 + H_2O \rightarrow 2HNO_3 + NO$

The second version of Tyco's process incorporates two changes aimed at reducing these very large thermal requirements thereby improving process economics. The first change involves running the absorber isothermally at a temperature of about 250°F. At this temperature the vapor pressure of water above the 80% sulfuric acid scrubbing solution just about equals the partial pressure of water in the flue gas. Consequently, moisture from the flue gas will not condense in the acid and will not have to be stripped from it. The second change further reduces the thermal requirement by substituting a catalytic $NOHSO_4$ oxidative decomposition step, operating at the same temperature as the scrubber, for the separate thermal decomposition and oxidation steps used in the other version of the process. Preliminary experiments made by Tyco indicate that activated carbon may be a suitable catalyst for the decomposition.

In either of the two Tyco processes, sufficient NO_2 must be recycled to the flue gas to oxidize the SO_2 to SO_3 and provide enough remaining to give a 1:1 NO_2:NO composition. Since the oxidation of SO_2 by NO_2 produces NO, two moles of NO_2 must be recycled for each mole of SO_2 in the flue gas to provide this equimolar NO/NO_2 product. Additional NO_2

$$2NO_2 + SO_2 \longrightarrow SO_3 + (NO + NO_2) \qquad (5\text{-}22)$$

must, of course, also be provided in the recycle to balance the NO present in the flue gas. The consequence of these requirements is that the total amount of NO_2 that must be recycled increases rapidly with both the SO_2 and NO contents of the flue gas as shown in Table 5-21. This places very stringent requirements on

Table 5-21

Effect of Flue Gas SO_2 and NO Concentration on Recycle Requirements of the Tyco Processes

SO_2 Content of Flue Gas, ppm	NO Content of Flue Gas, ppm			
	500	700	1000	1500
	NO_2 Recycle Requirements			
2000	4500	4700	5000	5500
3000	6500	6700	7000	7500

the scrubber efficiency. Considering the case of a typical flue gas produced by a coal fired power plant (Table 5-1) containing 2000 ppm SO_2 and 700 ppm NO, the total concentration of NO + NO_2 at the inlet to the scrubber will be 5400 ppm (4700 recycle + 700 original). If the scrubber is only 90% effective in Tyco's processes, 540 ppm or 77% of the original NO in the flue gas will not have been absorbed. Similarly at a scrubber efficiency of 95%, almost 39% of the original NO will not be absorbed. The removal efficiency becomes even worse with increasing SO_2 content of the flue gas and with decreasing purity of the recycle NO_2, (i.e, NO present in recycle). The extreme importance of having a very efficient scrubber in either of Tyco's processes is clearly apparent.

5.5.4. Complex Forming Salts

Nitric oxide is known to form complexes with a large number of compounds. Probably the best known of these are the ferrous sulfate and chloride complexes whose brown colors are the basis for nitrite and nitrate identification in the well known ring test. Excellent reviews of the nitrosyl complexes are provided by Moeller (5-84) and Addison and Lewis (5-85). Moeller classified the nitrosyl complexes into the six types shown in Table 5-22.

Table 5-22

Nitrosyl Complexes

Type of Complex	Examples
1 Nitrosyl Carbonyls	$Co(NO)(CO)_3$, $Fe(NO)_2(CO)_2$
2 $M^I(NO)_x A_y$ Complexes	
- Metal Nitrosyl Hydroxides	$Ni(NO)OH$
- Metal Nitrosyl Halides	$Fe_2(NO)_4I_3$, $Fe(NO)_2I$
	$Fe(NO)I$, $Fe(NO)_3Cl$,
	$Co(NO)_2$ X $Ni(NO)X$ X=Cl,Br,I
- Metal Nitrosyl Thio Compounds	$M[Fe(NO)_2S]$ $M=Na^+, K^+, NH_4^+$
	$M[Fe(NO)SSO_3]$ $M=Na^+,K^+,NH_4^+$
	$[Co(NO)_2(SSO_3)_2]^{-3}$
	$[Ni(NO)_2SSO_3)_2]^{-3}$
3 $M^{II}(NO)_xA_y$ Complexes	$Fe(NO)HPO_4$, $Fe(NO)SeO_4 \cdot H_2O$
	$Pd(NO)_2Cl_2$ $Pd(NO)_2SO_4$
4 $M^{III}(NO)_xA_y$ Complexes	$Fe_2(NO)_2(SO_4)_3$
	$B(NO)F_3$, $B(NO)Cl_3$
5 $[MA_5(NO)]^{\pm}$ Complex Groups	$[Mn(CN)_5(NO)]^{-3}$
	$[Fe(CN)_5(NO)]^{-2}$
	$[Ru(CN)_5)(NO)]^{-2}$
	$[Co(NH_3)_5(NO)]^{+2}$
	$[Ni(NH_3)_5(NO)]^{+1}$
	$[RuCl_5(NO)]^{-2}$
6 Miscellaneous Nitrosyl Complexes	$M_2SO_3 \cdot 2NO$
	$M[Fe_4(NO)_7S_3]$
	$M = Na^+, K^+$

where M is a cation, A is an anion of the complex.

In contrast to NO, few NO_2 complexes are formed. The best known NO_2 complex is $Co(NO_2)^=$ which can be precipitated as the potassium salt.

Little information is available on the use of complexing solutions to remove NO from gases. Gehlen discusses the reaction of NO with alkali sulfites (5-86) and hyposulfites (5-87) and a Linde patent (5-88) claims the use of alkali sulfite solutions for removing NO from coke oven gas. Jordan, et al (5-63) claim, however, that such absorption was far too slow for practical use.

The most complete study to determine the NO complexing capacity and rate was made by Ganz and Mamon (5-89) for $FeSO_4$ solutions. They found that $FeSO_4$ and $FeCl_2$ solutions had capacities at least ten times greater than those of $CoSO_4$, $NiSO_4$, $CuCl_2$, and $MnCl_2$. The addition of small amounts of sulfuric acid (0.5 to 1.5%) was found to inhibit the oxidation of the ferrous salts, while not having much of an effect on the stability of the nitrosyl complex. Pozin et al (5-90) in a later study of NO complexes measured the absorption capacity of $CuSO_4$, $CuCl_2$, $MnSO_4$, H_3PO_4, $CoSO_4$, $NiSO_4$, $Cu_2(NH_3)_nCl_2$ Na_2SO_3, $FeSO_4$ and $FeCl_2$ solutions. They too found $FeSO_4$ and $FeCl_2$, along with $Cu_2(NH_3)_n Cl_2$ and Na_2SO_3 to be the best absorbents, but their research capacities were considerably lower than those obtained by Ganz and Mamon. Pozin, et al, also found the NO absorption by Na_2SO_3 to occur irreversably. Earlier work by Pound (5-91) had also shown the inhibiting effect sulfuric acid had on the oxidation of ferrous salts. Such inhibition is desirable since ferric solutions do not complex NO.

Using the more optimisiic data of Ganz and Mamon, the amount of $FeSO_4$ solution needed to absorb nitric oxides from a typical flue gas was estimated. For these estimations it was assumed that a 20% $FeSO_4$ solution is used and is continuously circulated between a NO absorbing tower at a temperature of about 120°F. and a NO stripping tower operating at 200°F. To remove seventy percent of the nitric oxide (at the 700 ppm level) from the flue gas of a 1000 MW power plant, 15 x 10^6 gph of solution would have to be circulated. The calculations assume no kinetic limitations, i.e., equilibrium saturation of the solution is achieved in the absorber. The very high solution circulation rates required by this system result from the low complexing capacity of the solutions. In an actual system, where there would also be kinetic limitations, even greater circulation rates would be required. Furthermore, all the reported absorption data were obtained in the absence of oxygen, CO_2, and SO_2. The CO_2 and SO_2 would almost certainly lower the NO complexing capacity of the $FeSO_4$ solution, while the O_2 might destroy it completely by oxidizing the NO to NO_2 and the ferrous sulfate to ferric sulfate.

5.5.5. Organic Solutions

Organic liquids which dissolve or react with NO could be used as absorbents in a flue gas emission control process provided they met certain criteria. An acceptable material would have to have reasonable capacity for nitrogen oxides, would have to be stable to oxidations, must not present a serious fire or explosion hazard, must be very inexpensive or nearly totally regenerable, and must have low volatility. Low volatility is important for two reasons. First, evaporation losses from the scrubber must be made up, and second, solvent evaporation can change an NO_x pollution problem into an organic vapor pollution problem. An organic liquid having a vapor pressure of 500 μ at temperatures prevailing in the absorption tower (e.g. 120 to 150°F) for example, will produce a vapor emission of about 650 ppm in the stack gases - equivalent to a solvent loss of 4700 lb-moles/day for a 1000 MW power plant.

Classes of organic materials which are known to absorb nitrogen oxides include amines, ethers, alcohols and esters and polar aprotic solvents. Amines, as a class, are able to form addition compounds with NO_2 and NO/NO_2 mixtures, but these reactions are not "clean" and the by-products are generally non-regenerable. At high temperatures, amines, like NH_3 act as reducing agents for nitrogen oxides (5-38). At low temperatures Lovejoy and Vasper (5-92) report that reaction of aliphatic and aromatic amines with N_2O_3 produce nitrosamine by-products in addition to the amine nitrite. Whereas the amine nitrite can be regenerated by treatment with a strong base or with steam, the nitrosamine cannot. Lovejoy and Vasper also found that diazonium nitrites were the principal products of reactions involving primary aromatic amines while aliphatic amines decomposed the N_2O_3 to nitrogen. In a NAPCA-sponsored study at A. D. Little (5-93) amines were also found to be degraded when used for SO_2 absorption and were judged unsatisfactory for use in a flue gas SO_2 scrubbing process.

Ganz and Mamon (5-89) evaluated amyl acetate, dimethylaniline, isoamyl alcohol, amyl ether and ethanol amine for NO absorption. They concluded that these compounds were of no practical value because of their low absorption ability (i.e., lower than $FeSO_4$ solutions).

Maury and Nahill (5-94) claim the use of aqueous solutions of electron donor solvents such as tri-n-butyl phosphate, dimethyl formamide, triethylene glycol, dimethyl ether, dimethyl sulfoxides, and hexamethyl phosphoramide for scrubbing nitrogen oxides and nitric acid vapor. For an equimolar mixture of NO and NO_2 at low partial pressures, they show the equilibrium absorption capacities of these solutions to be about 100 times that of water. Although these particular solvents are too volatile to be used for scrubbing of stack gases, a possibility exists of synthesizing similar type higher molecular weight compounds with low vapor pressures which could be potential absorbents in a flue gas process. The probability of finding such materials, however, is judged to be too low to merit any research.

5.6 NO OXIDATION

It was pointed out in preceding sections of this report that alkali solutions, concentrated sulfuric acid and certain solids adsorbents, while unable to remove NO from gases, are able to remove NO and NO_2 in equimolar proportion. Since nitrogen oxide emissions from combustion equipment are predominantly in the form of NO, control of these emissions with alkali or sulfuric acid scrubbing requires some means of raising the average oxidation level of the nitric oxides to the equivalent of N_2O_3. Two methods of doing this have been considered in this study. The first is direct oxidation of NO in the flue gas. The second is recycle to the flue of NO_2 produced by regenerating the sorbent.

5.6.1 Direct Oxidation

Nitric oxide is oxidized by air (O_2) to nitrogen dioxide, but with low NO concentrations, the termolecular non-catalyzed reaction is very slow. Using published rate data (5-95), the residence time required for converting half of the 700 ppm NO found on the average in flue gas with the available flue gas oxygen (about 3%) is calculated to be about 33 minutes at a temperature of 120°F. At higher temperatures, this reaction is even slower. (5-96, 5-97).

The reaction time can be decreased somewhat by injecting additional air into the flue gas to increase the O_2 concentration. Since such addition also lowers the NO concentration, and the rate of oxidation varies with the square of the NO concentration (i.e., rate of oxidation = $k\,[NO]^2\,[O_2]$), there is an optimum dilution at about 30% air. At this optimum, the reaction time calculated as before becomes about 18 minutes, but this is still several orders of magnitude above what is practical for flue gas conversion.

Practical reaction times can be achieved using ozone as the oxidant. Based on published rate data (5-98), calculations show that half the NO could be oxidized in .0035 seconds using only 5% excess ozone. At a cost of about 15¢/lb., however, the cost of the ozone required in a power plant would be equal to about $2/ton of coal burned. This assumes that neither the O_3 nor the NO_2 formed reacts with SO_2 via reactions (5-23) and (5-24). Since this is unlikely, actual O_3 requirements would be greater.

$$SO_2 + NO_2 \longrightarrow SO_3 + NO \qquad (5\text{-}23)$$

$$SO_2 + O_3 \longrightarrow SO_3 + O_2 \qquad (5\text{-}24)$$

The catalytic oxidation of NO has been studied by a number of investigators. Burdick (5-95) found charcoal to be the most effective NO oxidizing catalyst of the materials he tested--Table 5-23. Kircher and Hougen (5-99) found activated carbon to be more active and less sensitive to moisture than silica gel. Based on these findings, Chu and Hougen (5-100) used activated carbon as the catalyst in a paper design study of an optimized catalytic nitric oxide reactor.

Table 5-23

Activity of NO Oxidation Catalysts Evaluated By Burdick

Catalyst	Temp. °C	Gas Comp.[(a)] NO %	O_2 %	H_2O %	3rd Order Rate Constant k'[(b)]
Glass container empty	0	3.11	20.4	0.1	21
	25	2.91	20.4	0.1	11
Crushed glass	25	2.82	20.4	0.1	12
	50	3.45	20.3	0.1	15
Untreated pumice	25	2.97	20.4	0.1	13
Pumice impregnated					18
with tungstic acid in HNO_3	50	3.06	20.4	0.1	21
	50	3.20	20.3	0.1	18
with tungstic acid in soln. of hydrogen peroxide	25	3.04	20.4	0.1	17
with NiO	25	3.00	20.4	0.1	16
with CoO	25	2.86	20.4	0.1	15
with metallic Ni	25	3.07	20.4	0.1	19
with metallic Co	25	3.02	20.4	0.1	19
with MnO_2	25	2.98	20.4	0.1	15
Platinized pumice	25	2.97	20.4	0.1	17
Platinized asbestos	25	2.02	20.4	0.1	17
Coke	25	2.02	20.4	0.1	20
Common charcoal	25	2.98	20.4	0.1	19
Coconut charcoal	25	1.33	2.96	0.1	10,000
	25	1.39	2.96	0.1	12,000
	80	1.63	2.59	0.1	8,800
	25	1.87	2.94	1.0	1,400
	25	1.86	2.04	1.0	1,100
	25	1.77	2.94	1.0	930
	50	1.31	2.96	1.0	1,350
	80	1.96	2.90	1.0	2,650
Peach-kernel charcoal	80	1.87	2.90	1.0	2,010
	80	1.71	2.90	1.0	2,130
	80	1.23	2.79	5.7	2,710
	80	2.22	2.70	5.6	3,110
	55	1.79	2.66	5.8	1,590
	55	1.66	2.80	5.7	1,165
	53	1.51	2.78	5.7	808
	53	1.59	2.77	5.7	910
	53	1.66	2.78	5.7	765
	100	1.27	2.45	14.7	3,440
Steamed coke	80	2.63	2.81	3.9	329

Footnotes on next page.

(a) Mole %, balance N_2

(b) For differential form of rate eq. $-\frac{dC}{dt} = k(C')(C)^2$

Integrated form of rate eq. -

$$k't = \left[\frac{1}{2C'_i - C_i}\right]\left[\frac{1}{C} - \frac{1}{C_i}\right] - \frac{2.3}{(2C'_i - C_i)^2}\log_{10}\frac{(2C'_i - C_i + C)C_i}{2C'_i - C} \qquad (5\text{-}25$$

where C_i = initial conc. of NO, mole %

C = conc. of NO at time t, mole %

C'_i = initial conc. of O_2-mole %

C' = conc. of O_2 at time t, mole %

t = reaction time in seconds

k' = 1/2 k, sec^{-1} (mole $\%)^{-2}$

Based on Burdick's data with a rate constant, k, of 3000 for peach-kernel charcoal (6% moisture in the gas), calculations show that half of the NO at a 700 ppm level can be oxidized in about 8 seconds. With SO_2 in the gas able to consume NO_2 by reaction (23), even longer reaction times are needed to achieve a final oxidation level equivalent to N_2O_3. Although 8 seconds represents more than a hundredfold decrease for the reaction time required for the uncatalyzed reaction, it is still much too long. Thus, for a 1000 MW power plant, a char-filled reactor would have to have a volume of about 1.2×10^6 ft^3 to provide such residence time.

5.6.2 NO_2 Recycle

The equimolar NO_2-NO ratio can be achieved by recycling NO_2 back to the flue gas. The recycle NO_2 can be obtained from the spent sorbent used to remove the nitrogen oxides from the flue gas.

First, the sorbent would be decomposed to yield a concentrated stream of NO. In the case of alkali or caustic flue gas scrubbing, the nitrites formed could be decomposed either thermally or by addition of strong acid. The reactions involved in such decomposition are shown below for $Ca(NO_2)_2$. Solid nitrate-forming sorbents could be similarly

Thermal Decomposition

$$3Ca(NO_2)_2 \xrightarrow{\Delta} Ca(NO_3)_2 + 2CaO + 4NO \qquad (5\text{-}26)$$

$$Ca(NO_3)_2 \xrightarrow[\text{Higher Temperature}]{\Delta} CaO + 2NO + 3/2\ O_2 \qquad (5\text{-}27)$$

Acid Decomposition

$$3Ca(NO_2)_2 + 2H_2SO_4 \longrightarrow Ca(NO_3)_2 + 2CaSO_4 + 4NO \qquad (5\text{-}28)$$

$$Ca(NO_3)_2 + H_2SO_4 \longrightarrow CaSO_4 + 2HNO_3 + 2H_2O \qquad (5\text{-}29)$$

decomposed. The NO obtained would then be oxidized by air to NO_2. The reactor required for this oxidation would be much smaller than that required for the direct oxidation of dilute nitric oxide in the flue gas.

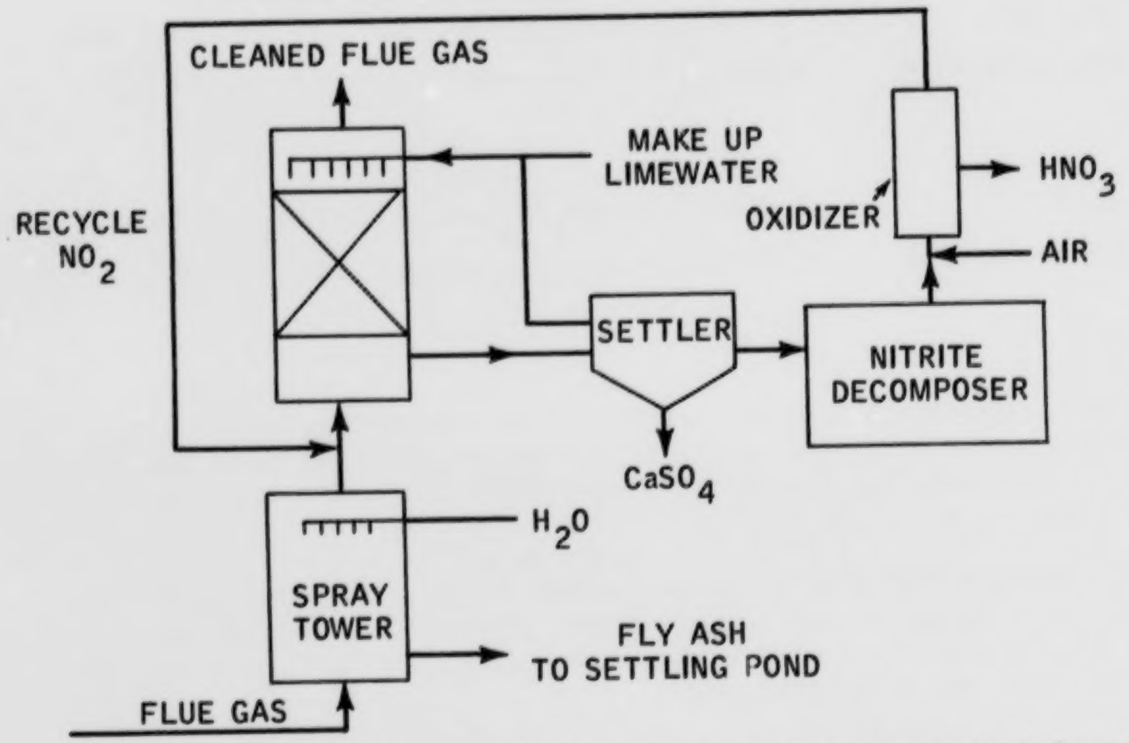
For an SO_2-free gas, the amount of NO_2 recycled would be approximately equal to the amount of NO present in the flue gas. With SO_2 in the gas, additional NO_2 may have to be recycled since NO_2 can react with SO_2 via reaction (5-23).

In Tyco's flue gas treating process, complete SO_2-NO_2 reaction is assured by adding the NO_2 to the flue gas at a temperature of about 300°F. Table 5-21 shows that under these conditions the amount of NO_2 recycled must be many times the amount of NO present in the flue gas. On the other hand, for NO_2 recycle processes where SO_2 oxidation is not required, the NO_2 should be added to the flue gas at as low a temperature as possible. This would suppress the SO_2-NO_2 reaction and promote the NO-NO_2 reaction to N_2O_3.

Figure 5-17 shows the outline of a potential NO_2 recycle scrubbing system using limewater as the absorbent. A spray tower is used in this process to cool the flue gas and remove fly ash. Following injection of the NO_2 into the cooled flue gas, the flue gas is scrubbed to remove sulfur and nitrogen oxides.

Figure 5-17

POTENTIAL LIMEWATER SCRUBBING SYSTEM

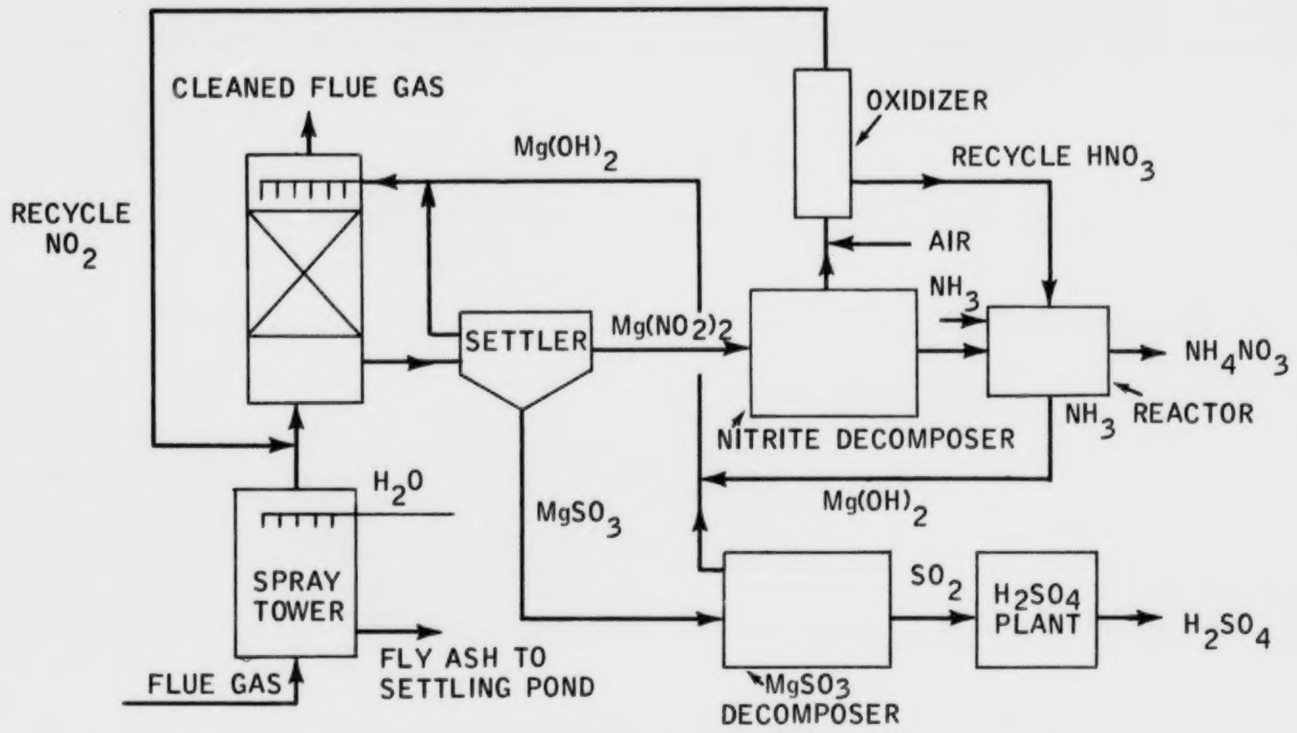


Precipitated calcium sulfite and sulfate are separated from the effluent scrubbing solution containing the calcium nitrite. The calcium nitrite is decomposed and the NO produced oxidized to NO$_2$ for recycle to the scrubber and to HNO$_3$. Complete decomposition is accomplished by evaporating the calcium nitrite solution and then raising its temperature to about 1300°F. The CaO formed by the decomposition is returned to the scrubber along with make-up lime. Alternately, the Ca(NO$_2$) solution can be acidified with H_2SO_4 to liberate NO and precipitate additional $CaSO_4$. If just cooling of the flue gas is insufficient for inhibiting the SO_2-NO_2 reaction, two separate scrubbers can be used, the first for removing SO_2 and the second for removing the N_2O_3. NO$_2$ would of course then be recycled to the cooled flue gas between scrubbers.

Figure 5-18 shows a second potential NO$_2$ recycle scrubbing system using a Mg(OH)$_2$ scrubbing liquor as the absorbent. Such a process has been described by Schmidt et al (5-75) for removing nitrogen oxides from nitric acid plant tail gas. The use of Mg(OH)$_2$ provides two advantages over limewater. First, the insoluble $MgSO_3$ formed by reaction with SO_2 can be separated from the Mg(NO$_2$)$_2$ solution and decomposed separately to yield a concentrated SO_2 stream from which sulfuric acid can be produced. Second, the Mg(NO$_2$)$_2$ can be decomposed in solution under pressure at considerably lower temperature than is possible for Ca(NO$_2$)$_2$ This decomposition is not complete and yields Mg(NO$_3$)$_2$ in addition to NO. The Mg(NO$_3$)$_2$ solution can be treated with NH_3, however, to yield NH_4NO_3 and Mg(OH)$_2$. The Mg(OH)$_2$ together with the MgO formed from the decomposition of the $MgSO_3$ would be returned to the scrubber. The Mg(OH)$_2$ process would thus yield two salable products, H_2SO_4 and NH_4NO_3, to offset process costs. This process requires the formation of insoluble $MgSO_3$ rather than $MgSO_4$. To inhibit $MgSO_4$ formation, the scrubber pH would be maintained on the basic side.

Figure 5-18

POTENTIAL $Mg(OH)_2$ SCRUBBING SYSTEM


CLEANED FLUE GAS
RECYCLE NO2
Mg(OH)2
OXIDIZER
RECYCLE HNO3
AIR
NH3
SETTLER
Mg(NO2)2
NH4NO3
NH3
REACTOR
NITRITE DECOMPOSER
H2O
MgSO3
Mg(OH)2
SPRAY TOWER
SO2
H2SO4 PLANT
H2SO4
FLY ASH TO SETTLING POND
FLUE GAS
MgSO3 DECOMPOSER

5.7 PHYSICAL SEPARATION OF NO_x

Differences in physical properties can often provide the basis for separating one of the components of a gas mixture from the others. Physical separation techniques include condensation, diffusion, permeation, centrifugation and the use of electric and magnetic fields.

Table 5-24 lists some of the physical properties of NO. All of these properties fall within the range of the corresponding properties of the other components of the flue gas making physical separation very difficult.

Table 5-24

Physical Properties of NO

Mol. Weight	30.008
Normal Melting Point	109.49°K
Normal Boiling Point	121.36°K
Liquid Vapor Pressure	$\log_{10} \text{Pcm} = \frac{-776}{T} - .002364\,T - 8.562128$

T = °K

Δ H vaporization @ 121.36°K = 3,292.6 cal/gr. mole

Magnetic Susceptibility

@ 20°C = 1.46×10^{-3}
(NO is Paramagnetic)

5.7.1 Condensation

Condensation is an impractical method of removing NO from flue gases. Table 5-25 shows the temperatures at which various components of typical flue gas would start condensing if the gas was refrigerated. In order to cool the huge volume of flue gas from a power plant to a temperature of -315°F, the requirements in energy and heat exchange surface would be prohibitive. In a study completed under NAPCA contract (Ph 22-68-34), Westinghouse (5-101) concluded that condensation was even an impractical method for the separation of SO_2 from flue gas and this separation is easier than that of NO.

Table 5-25

Condensation Temperature of Flue Gas* Components

Flue Gas Components	Volume %	Saturation Temp. °F
N_2	76.2	-321
CO_2	14.2	-147
H_2O	6.0	97
O_2	3.3	-344
SO_2	0.2	-147
NO	0.07	-315

* Produced in a typical coal fired plant (see Table 5-1)

5.7.2 Magnetic Separation

The nitric oxide and oxygen in the flue gas can potentially be concentrated by the application of a strong magnetic field since both gases are paramagnetic. Such a magnetic field would tend to enduce selective diffusion of NO and O_2 in the direction of the field. Westinghouse, in the study cited above, concluded that magnetic fields of the order of 10^4 Oersted would be required to achieve maximum diffusional effects in the absence of gas turbulence, but that a field strength a thousand times higher would be required with the kind of turbulence experienced by the flue gases. Field strengths of this magnitude are currently used only as research tools and require enormous amounts of energy to produce.

5.7.3 Diffusion and Membrane Permeation

Diffusion of gases through porous media can be used as a separations technique when the gases to be separated differ in molecular weight. Under ideal conditions diffusion takes place by Knudson flow. With a molecular weight close to and in between those of O_2 and N_2, diffusional separation of NO would require a very large number of contact stages. For the much easier diffusional separation as SO_2 (MW = 64), Westinghouse (5-101) concluded that control of SO_2 emissions in a 500 MW power plant would cost $490 million a year.

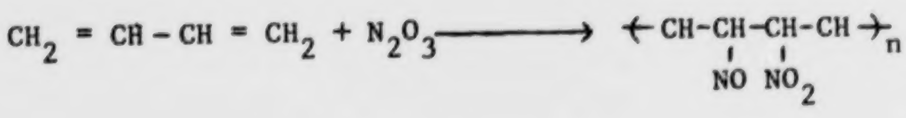
Membrane permeation can be used to separate gases when the gases exhibit different solubilities in the membrane material. The difference in partial pressure of the diffusing gas on the two sides of the membrane provides the transport driving force. This difference can be provided by operating with an actual pressure difference or by operating at the same pressure and using a sweep gas on the product side of the membrane.

General Electric, working under contract to NAPCA (Ph 86-68-76), researched the use of an immobilized liquid membrane barrier for desulfurizing flue gas and concluded that such a membrane process was too costly for this purpose (5-102). Using their best membrane, one containing polyethylene glycol, investment costs for SO_2 control in a 1000 MW plant were calculated to be over $33 million, and since it is unlikely that a working liquid would be found in which NO is more soluble than is SO_2 in polyethylene glycol, plant costs for NO control would be even higher.

5.7.4 Electric Corona Discharge Precipitation

Electric discharge precipitation was successfully used to remove NO from manufactured gases. Such removal was used to prevent formation of "vapor-phase" gum deposits resulting from the reaction of nitric oxides and organic compounds - principally unsaturates. Shively et al (5-103) describe the use of an electric treater consisting of a pair of electrodes, one a plane plate and the other a plate containing many sharp points. Operating with an electrode potential difference of about 10,000 volts, power consumption was about $20 kwh/10^6 ft^3$ gas treated. Nitric oxide concentration was reduced by over 97% from an average initial level of about 0.5 ppm. with contact times of less than a second.

For the treatment of power plant flue gas, power consumption of $20 kwh/10^6 ft^3$ would amount to less than 0.2% of the plant's output. This power requirement is modest but it appears that unsaturated hydrocarbons are essential for NO removal (5-104) by electron discharge precipitation, and that the process involves chemical rather than physical removal. Presumably, the electric discharge forms ozone, which promotes the oxidation of NO to N_2O_3 (i.e., NO + NO_2) which then reacts with olefinic hydrocarbons, particularly those possessing conjugated double bonds.



$$\mathrm{CH_2 = CH - CH = CH_2 + N_2O_3 \longrightarrow \left(CH-\underset{NO}{CH}-\underset{NO_2}{CH}-CH \right)_n} \qquad (5\text{-}30)$$

In effect, the electric discharge precipitator greatly accelerates the formation of gum which it then removes. Thus Baum et al (5-105) propose a method of purifying gases containing NO and olefins by adding NO_2 to the gas mixture in amounts ranging from .3 to 1.0 the amount of NO present.

Since power plant flue gases do not contain any significant quantities of unsaturates, the application of the electrostatic precipitation technique to NO emission control would undoubtedly require adding such compounds to the gas. Even if this didn't represent a potential hydrocarbon emission problem, raw material costs would be too high. The use of butadiene for example, at an assessed delivered price of 10¢/lb., would alone add over $1.60/ton coal burned to the cost of producing power.

5.8 SUMMARY OF HIGHLIGHTS

This study of potential technology for the control of nitrogen oxide emission by combustion flue gas treatment has shown that:

- There are currently no established gas treating processes for NO_x control that are directly applicable to control emissions from power plants.

- No effective catalyst is available for use in a potentially simple, low investment NO decomposition process, and the possibility of finding such a catalyst with further R&D appears low. The use of certain alkali or alkaline additives in conjunction with fluidized bed combustion systems does show some promise.

- Selective reductions of NO by NH_3, H_2S and H_2 appear much more likely possibilities and have been demonstrated under laboratory conditions. The use of NH_3 and H_2S would permit control of SO_2 emissions as well. Research is needed to find catalysts acceptable from the standpoint of cost, life, and activity.

- Such common adsorbents as silica gel, alumina, molecular sieves, char and ion exchange resins appear capable of oxidizing and then adsorbing nitric oxides. Capacities vary but all are low at the concentrations at which NO is found in flue gas. The presence of H_2O, CO_2 and SO_2 further reduces capacity. These adsorbents are judged to be unlikely candidates for use in an adsorption process. Certain metal oxides, particularly manganese and treated ferric oxides, may be acceptable adsorbents, especially in a regenerative system with recycle of NO_2 to the flue gas.

- Aqueous scrubbing systems employing alkaline solutions or concentrated sulfuric acid appear to offer the most potential for simultaneous control of nitrogen and sulfur oxides emissions in flue gas. These systems require equimolar concentrations of NO and NO_2 to be effective. The homogeneous or catalytic oxidation of NO in flue gas is either too expensive or too slow to achieve equimolar concentrations. Recycle of NO_2 to the flue gas appears to offer the best possibility for doing this. The recycle NO_2 can be obtained by oxidizing the concentrated NO stream made by the thermal, catalytic, or chemical decomposition of the absorbent.

- NO removal from flue gas based on differences in physical factors such as molecular size, condensation temperature and magnetic susceptibility of the components appears very improbable.

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6. CONTROL OF NO_x EMISSIONS FROM NON-COMBUSTION SOURCES

The economic necessity of recovering NO_x formed in the manufacture and uses of nitric acid has led to a large amount of chemical research which is applicable to problems in NO_x control. It must be recognized, however, that most of this research has been for the recovery of NO_x at about 3000 ppm in the tail gas. Therefore, this is not the same problem as the removal of NO_x from stack gases at much lower concentration levels. The principal processes developed are discussed below.

6.1. NITRIC ACID MANUFACTURE

A large body of technology has been developed for treating tail gas from nitric acid plants. Catalytic reduction is particularly suited to the nitric acid manufacturing process, and various systems have found wide-spread commercial use. Caustic scrubbing removes NO_x, but there are few commercial applications due to problems at many locations in disposing of the spent caustic. Molecular sieve adsorption shows promise, and is now offered for commercial use with moisture-free gases(6-1, 6-2). Absorption in concentrated sulfuric or nitric acid has been investigated(6-3), but does not appear competitive.

Catalytic reduction is particularly applicable to the pressure process because the reactor can be placed in the tail gas circuit after the preheater. Energy generated by the reaction of fuel with oxygen and nitrogen oxides is recovered in the turboexpander, increasing power recovery. Thus, the expander may provide most of the power required by the air compressor(6-4, 6-5).

Chemical Construction Corporation, which first developed a catalytic reduction system, points out that "our initial efforts were fortuitous in that we developed the catalytic combustion system basically as an improved means for recovering energy, and achieved the decolorization of the stack gas as a welcome side effect."(6-6)

Several types of catalytic reduction units have been used with varying degrees of success. All employ fuel to reduce nitrogen oxides, converting NO_2 to NO and NO to N_2. Non-selective reduction uses hydrogen, hydrocarbons, or carbon monoxide(6-7) as fuel, which reacts with oxygen in the tail gas, as well as with the nitrogen oxides. Selective reduction uses ammonia which reacts selectively with NO_x, in preference to molecular oxygen. In all catalytic reductions, catalyst activity decreases more or less with use.

6.1.1. Non-Selective Catalytic Reduction of NO_x

Non-selective reduction units include those designed for decolorization and energy recovery, and also units designed for NO_x abatement. Decolorization and power recovery units reduce NO_x to NO and burn out part of the oxygen, but NO reduction to molecular nitrogen is limited. The purpose of non-selective abatement units is to reduce the NO also.

In non-selective reduction, the following reactions take place when a preheated mixture of tail gas and methane pass over the catalyst.

$$CH_4 + 4NO_2 \longrightarrow 4NO + CO_2 + 2H_2O \tag{6-1}$$

$$CH_4 + 2O_2 \longrightarrow CO_2 + 2H_2O \tag{6-2}$$

$$CH_4 + 4NO \longrightarrow 2N_2 + CO_2 + 2H_2O \tag{6-3}$$

Similar equations can be written substituting hydrogen for methane; 4 moles of hydrogen are needed to replace one mole of methane.

The kinetics are such that reduction reaction (6-1) is faster than reduction reaction (6-2) but abatement reaction (6-3) is much slower than reaction (6-2). Thus, decolorization can be accomplished by adding only enough fuel for partial oxygen burnout. But if NO_x abatement is required, sufficient fuel must be added for complete oxygen burnout.

Catalytic reduction units for decolorization and power recovery are used in about 50 nitric acid plants in the U.S.(6-5). Many use natural gas for fuel, while some use hydrogen. When natural gas is used, it is necessary to preheat the tail gas to about 900°F to insure ignition. Preheat temperatures as low as 300°F will insure ignition with hydrogen(6-7).

Catalytic reduction is highly exothermic. The temperature rise with methane is about 230°F for each percent oxygen burnout, and with hydrogen about 270°F(6-4). For decolorization, the outlet temperature is ordinarily limited to 1200°F, the maximum temperature limit of turboexpanders with current technology(6-8). Increased power recovery may justify adding sufficient methane to reach the temperature limit of the turbine.

Supported platinum or palladium catalysts are employed in decolorization. Catalyst supports include ceramic spheres, ceramic pellets, ceramic honeycomb, and woven nichrome ribbon. The honeycomb structure is reported to give low pressure drop at the high space velocities of 100,000 V/H/V. In new decolorization units, honeycomb supports are favored over ceramic spheres and pellets which require lower hourly space velocities of 30,000 V/H/V(6-9, 6-10, 6-11).

At a given level of NO_2 removal, the nichrome-supported catalyst is said to convert more NO to N_2 than the ceramic supported catalyst, and uses more fuel(6-8).

Both catalyst and nitric acid manufacturers report satisfactory performance for decolorization units. The reduction of total NO_2 + NO is limited, but ground level NO_2 concentration in critical areas near the plant is reduced substantially(6-8).

Non-selective catalytic abatement is more difficult technically than decolorization, and commercial results have been less satisfactory. Provisions must be made to control the heat released in burning out all the oxygen from the tail gas, which must be done before extensive NO reduction may take place.

As mentioned above, the tail gas must be preheated to 900°F to insure ignition when using methane. Outlet temperatures would reach 1370°F and 1590°F for 2 and 3% oxygen burnout, respectively. These temperatures compare to the 1200°F maximum temperature limit for current turboexpanders and the 1500-1600°F maximum limit for catalysts. For single-stage operation, oxygen in tail gas cannot exceed 2.6% to remain within the temperature limit of the catalyst, and cooling must be provided to meet the turboexpander limit. Older turbines may have even lower temperature limitations.

Two or three plants are known to have installed single-stage non-selective abators. They are believed designed for natural gas(6-8). As noted above, oxygen concentration cannot exceed about 2.6%. The reactors must be designed to withstand 1500-1550°F at 100-120 psig, which requires costly refractories or alloys. Ceramic spheres are used as catalyst supports, at hourly gas space velocities up to 30,000 V/Hr/V for NO_x levels of 100-300 ppm max., depending on catalyst age and gas rate(6-8). Effluent gas must be cooled by heat exchange or quench to meet the temperature limitation of the turbine. It would be logical to use a waste heat boiler to generate steam.

A somewhat cheaper, but less successful alternative is two-stage reduction. Two or three such commercial installations are known in the U.S. One system involves two reactor stages with interstage heat removal(6-11). Another two-stage system involves preheating 70% of the feed to 900°F, adding fuel and passing the mixture over the first-stage catalyst. The fuel addition to the first-stage is adjusted to obtain the desired outlet temperature. The remaining 30% of the tail gas, preheated to only 250°F, is used to quench the first-stage effluent. The two streams plus the fuel for complete reduction are mixed and passed over the second-stage catalyst, and the effluent passes directly to the turboexpander. This system avoids high temperatures and coolers, or waste heat boilers (6-7, 6-12, 6-13, 6-14).

Honeycomb ceramic catalysts have been employed in two-stage abatement, with hourly gas space velocities of about 100,000 in each stage(6-10).

Commercial experience with single-stage catalytic abators has been satisfactory, while two-stage units operating on natural gas have not been as successful. Single-stage units can be designed for NO_x levels as low as 100-300 ppm. Two-stage units designed for abatement have frequently been able to achieve abatement for periods of only a few weeks, at which point declining catalyst activity results in increasing NO levels. Recent data indicate that successful abatement can be maintained for somewhat longer periods. However, the units continue to serve for energy recovery and decolorization(6-8).

The success of the single-stage abator compared to the limited success of the two-stage units may result from the following factors: the catalyst is in a reducing atmosphere, the temperatures are higher, and spherical rather than honeycomb catalyst supports are used. It has not been practical to change catalyst type in two-stage units because the reactors designed for a space velocity of 100,000 V/Hr/V would be too small to accommodate the spherical catalyst which effectively removes NO at a space velocity of about 30,000. The failure of the honeycomb catalyst in NO reduction service compared to its success in decolorization may reflect the fact that reaction kinetics make it much more difficult to reduce NO than NO_2(6-8).

Fuel requirements are 10-20% over stoichiometric for nonselective abatement when using methane. Some hydrocarbon and CO appear in treated tail gas. Not all of the methane is converted in decolorization. Less excess fuel is required when hydrogen is used(6-8).

6.1.2. Selective catalyst abatement must be carried out within the narrow temperature range of 410°F to 520°F. Within these limits, ammonia will reduce NO_2 and NO to molecular nitrogen, without simultaneously reacting with oxygen. The reactions are shown in the following equations:

$$8NH_3 + 6NO_2 \longrightarrow 7N_2 + 12H_2O \qquad (6\text{-}4)$$

$$4NH_3 + 6NO \longrightarrow 5N_2 + 6H_2O \qquad (6\text{-}5)$$

Above 520°F, ammonia may oxidize to form NO_x and below 410°F, it may form ammonium nitrate(6-4).

Three commercial plants have installed selective abatement units. Performance to date has ranged from unsatisfactory to partly successful. The reaction supplies little energy for recovery in the turboexpander(6-8).

A number of World War II nitric acid plants of 55 T/D capacity are equipped with reciprocating expanders for power recovery. Installing selective abators upstream of these expanders could result in ammonium salts entering the lube oil system, and may lead to explosions. This is not a problem with turboexpanders.

Platinum on a honeycomb support is used in selective abatement. This catalyst system has not been very successful up to the present time, so nitric acid manufacturers feel that selective abatement is not yet commercially developed(6-8). Platinum on pellets may be satisfactory for this service(6-10). The very high cost of platinum catalysts and the necessity of using them only on a gas stream which is essentially free of sulfur compounds excludes their use from combustion flue gas treatment.

6.1.3 Alkaline scrubbing is an alternative method of removing NO_x from nitric acid tail gas. Sodium hydroxide, sodium carbonate, ammonium hydroxide, or calcium carbonate react with NO_x to form nitrite and nitrate salts. Examples of NO_x removal levels up to 90% have been reported in the literature (6-15). The high removal levels probably reflect a favorable NO/NO_2 ratio of about 1/1.

While sodium hydroxide or sodium carbonate scrubbing removes NO_x from tail gas, it has not found extensive use in the industry because of the difficulties encountered in disposing of the spent solution containing nitrite and nitrate salts, which become serious water pollutants, if released as a liquid effluent. The concentrations are too dilute for economic recovery of the salts (6-8).

6.1.4 Adsorption and Absorption Techniques

Several potential processes for tail gas treatment have been proposed which are still to be tested commercially. Molecular sieves have been reported to be much more effective adsorbents for NO_x in tail gas than silica gel (6-1, 6-2). They have recently become commercially available for this purpose and limited evidence indicates that they work well. The adsorbed NO_x can be desorbed as enriched NO_x or HNO_3 by displacement with hot air or steam, and returned to the nitric acid plant. Silica gel is probably more acid resistant than the zeolites.

NO_x can be absorbed in nitric acid or sulfuric acid. Sulfuric acid readily absorbs a 50/50 mixture of NO/NO_2. The tail gas contains water, also, which would dilute the sulfuric acid. Reconcentration makes sulfuric acid absorption costly.

Concentrated nitric acid would be expected to absorb some NO as well as the 50/50 mixture of NO/NO_2. Again, the abundance of water in tail gas would dilute the acid. Absorption of NO_x from tail gas using 20-35% HNO_3 followed by regeneration of the contaminated acid with oxygen has been proposed in the literature (6-3).

Emissions from storage tanks can be collected through a vapor recovery system and returned to the process feed, as can emissions from nitric acid concentration. Stainless steel is recommended in construction of the equipment. Frequently, emissions from this source are disposed of by incineration, which reduces the NO_x content by 75-90% (6-16). Fume incineration is covered in Section 6.2.3.

6.2 NITRIC ACID USES

Recovery of NO_x from streams discharged from processes consuming nitric acid is frequently practical as an economic necessity. Control methods employed are discussed below.

6.2.1 Ammonium Nitrate Manufacture

As discussed in Section 3.1.4, NO_x emissions from ammonium nitrate manufacturing are negligible, since a slight excess of ammonia is used in the neutralization to reduce product decomposition.

6.2.2 Organic Oxidations

In commercial operations, the economics require recovery of NO_x as nitric acid. The recovery is accomplished by mixing the off-gas with air and sending the stream to an absorbing tower, where nitric acid is recovered as the tower bottoms and non-recoverable N_2O and nitrogen pass overhead. The recovery system is similar to the NO oxidation and the absorption sections of a nitric acid plant, as described in Section 3.1.4.

Should these emission rates be considered too high, further reduction could be attempted by standard techniques such as incineration in a reducing flame (Section 6.3.1) or additional absorption.

Longer range, a potential control for eliminating NO_x from organic oxidation processing is the replacement of nitric acid as an oxidant by catalytic processes using air or oxygen. Most terephthalic acid is now produced using catalytic processes employing air oxidation. Laboratory catalytic air oxidation of cyclohexanol and cyclohexanone to adipic acid has also been reported (6-17) but no commercial processes are known.

6.2.3. Organic Nitrations

Both the rate and concentration of NO_x emission in off-gas from nitrations vary widely depending on the reaction carried out, equipment size, and whether batch or continuous processing is employed.

In large batch or continuous nitrations operations are carried out in closed reactors. Fumes are conducted from the reactor, air is added, and the mixture enters an absorption tower for recovery of nitric acid.

Non-condensable gas from acid denitration is treated in the same manner as reactor gas. A common absorber is sometimes employed. If the residual gas from the absorber still contains too much NO_2, it may be further reduced by conventional techniques such as caustic scrubbing or fume burning.

Small batch nitrators used in manufacturing specialities such as drugs and dyes are small volume, high intensity NO_x emitters. In one plant (6-18), reaction times ranged from 3 to 13 hours depending on the product made. From 3 to 850 batches of each product were made each year. Emissions ranged from 1.4 to 260 pounds of NO_x per ton of nitric acid, with a median rate of 42 pounds per ton of nitric acid. The median rate was 14 pounds per ton excluding one of the products. The emissions, which are vented to individual stacks, are high in NO_x concentration and brown in color for a few hours per batch, but low in pounds per day. No figures are available on concentration or emission rates in pounds per day.

The "off-on" character of emissions make them difficult to control and contribute to very high pollution abatement costs per ton of nitric acid consumed. Operating costs for such equipment would render approximately half of the small batch nitrations so uneconomical that the manufacture of these products would be terminated (6-18). Large batches may be suitable for conversion to continuous operating, but small batches are not.

Caustic scrubbing and fume incineration were said to be the most plausible controls for specialty batch nitrations. Catalytic reduction is usually ruled out because of organic and other impurities in the gas. Neither control is considered highly efficient in this application.

6.2.3.1. Fume Incineration

Fume burning is carried out under reducing conditions. An excess of fuel is used and NO_x, acting as an oxidant, is reduced to nitrogen. The system should have at least 10% excess fuel. Hardison discusses the fuel/oxidizer ratio limitations in his article (6-19). NO_x reductions of 75-90% are reported (6-16, 6-19). Burner designs are discussed in references (6-19) and (6-20).

6.2.3.2. Alkaline Scrubbing

Alkaline scrubbing is discussed in Section 6.1.3.

6.2.3.3. Urea Addition

A potential technique for control of NO_x emissions which is suitable for some chemical systems, but not others, is adding urea to the reactants. Urea reacts with N_2O_3 or nitrous acid to form CO_2 and nitrogen. In addition to suppressing NO_x formation, oxidation of hydrocarbons is virtually eliminated (6-21).

6.2.4. Explosives

NO_x is emitted in the manufacture of explosives as byproducts from nitration operations. The control of NO_x in nitration, including emissions from spent acid recovery is discussed in Section 6.2.3.

Other sources may include acid tanks, nitric acid concentration, denitration and redwater destruction. Controls include fume incineration, absorption with nitric acid recovery and caustic scrubbing, which are all discussed in preceding sections.

NO_x is sometimes generated in explosions. NO_x is minimized by use of oxygen-balanced or oxygen deficient explosives. Precautions should be taken to avoid exposure of personnel to NO_x fumes produced from underground explosions.

6.2.5. Other Uses of Nitric Acid

6.2.5.1. Phosphate Rock Acidulation

NO_x emissions from nitric acid acidulation of phosphate rock are probably reduced to only a minor degree in the water scrubbing employed for particulate and fluorides control.

One company has found the addition of urea to the acidulation mixture reduces NO_x emissions and eliminates the brown plume (6-22). Urea, as mentioned in the section 6.2.3.3. reacts with NO and NO_2 to form N_2.

6.2.5.2. Metals Treatment

Some of the metals treatment processes employing nitric acid are stainless steel pickling, chemical milling, bright dipping of copper, and solution of molybdenum cores used in manufacturing tungsten filaments. Control consists of proper hooding and ventilation, and sometimes methods for either reducing NO_x production or removing it from the off gas.

In nitric acid pickling of stainless steel treating equipment should be properly hooded and ventilated and the fumes scrubbed to protect workers. Urea addition would probably control NO_x emissions.

It has been reported that copper can be bright dipped in cold nitric acid alone when urea is added. A highly acceptable finish is obtained and NO_x fumes are eliminated. Sulfuric acid should not be used with the nitric acid-urea mixture since nitrourea, an explosive, can form. Not more than 8 ounces of urea per gallon should be added, and satisfactory operation can be obtained with only 2 ounces per gallon.

In chemical milling, addition of 6 to 8 ounces of urea per gallon of 40% nitric acid will reduce NO_2 emissions from 8000 ppm to levels below 10 ppm, provided a bubble disperser is used (6-23)

For the manufacture of light-bulb filaments, Decker (6-11) describes air pollution equipment for reducing the dense NO_2 fumes which are given off periodically when the cores are dissolved. The fumes pass over a charcoal adsorber bed, which adsorbs NO_x as fumes are generated and desorbs when no fumes are being generated. This smooths out peaks and valleys in NO_x content in off-gases which are then heated and combined with carbon monoxide and hydrogen from a rich combustion flame, and the mixture is passed through a bed of noble metal catalyst. A colorless gas is released from the equipment.

6.3. MINOR NON-COMBUSTION SOURCES

In this section welding, electrostatic precipitators, and silos will be discussed.

6.3.1. Arc Welding

Control consists in recognizing the potential hazard and providing adequate ventilation and dispersion into the atmosphere. Welding operations in which no visible fume exists should not be assumed to be free of NO_x.

6.3.2. Electrostatic Precipitators

If NO_x is formed in electrostatic precipitators, it can possibly be controlled by avoiding excessive arcing between electrodes. Section 5.7.4 discusses the available information on the effect of electrostatic precipitators on NO_x formation and decomposition.

6.3.3. High NO_x Levels in Silos

Control consists of recognizing the hazard, providing adequate ventilation, and limiting access to the immediate area until generation of the gas has ceased, and dissipation has taken place.

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7. PREVENTION OF URBAN POPULATION EXPOSURE TO HIGH LEVEL NO_x EMISSIONS

In this section, means other than engineering process control of preventing urban population exposure to NO_x emissions are discussed.

7.1. Fuel Switch

The type of fuel burned can have an important effect on NO_x emissions. In some installations it has been noted that gas firing produced roughly half the emissions of those prevailing when burning oil in the same equipment at an equivalent firing rate. This phenomenon is also evidenced in the average NO_x emission factor data published by the U.S. Public Health Service (7-1) for gas, oil and coal in various categories of equipment. A comparison of NO_x emissions between gas, oil and coal on an equivalent BTU basis is given in Table 7-1.

Referring to Table 7-1, it can be noted that NO_x emissions are highest with coal, intermediate with oil, and lowest with natural gas. Potentially, therefore, reductions in emissions could be effected by a fuel switch in a given piece of combustion equipment. For instance, converting an ordinary boiler designed for coal or oil firing to one burning natural gas could result in a reduction in NO_x emissions. The extent of the potential reduction is dependent on the design of the combustion equipment, the type of burners, the method of firing, the differences in emission factors between the fuels, etc. Also, it must be rementioned that wide variations in the emission factors listed in Table 7-1 could be expected in individual units. One conclusion of the California investigations in the early 1960's was that predictions of emissions in a given piece of equipment should not be made based on the emission data developed, since emissions in identical equipment under the same conditions often times vary widely. Therefore, the decrease in NO_x emissions which may be expected as a result of a fuel switch from a comparison of the data in Table 7-1 may not materialize.

The relationship of the emission data in Table 7-1 appears to apply to combustion equipment with firing rates under 5×10^9 BTU's per hour. At higher firing rates, in boilers serving turbine/generator units greater than 500 megawatts in size, emissions with natural gas firing can be considerably higher than with oil or than might be expected with pulverized coal. This can be noted in Figure 9-4 "Estimated NO_x Emission Rates--Composite Boilers," as discussed in further detail in Section 9. Therefore, in making a fuel switch to effect a lower NO_x emission, the size of the installation is also an important factor.

In California, switching from heavy fuel oil derived from California crude to a lower sulfur, paraffinic type fuel oil of Indonesian and Alaskan crude sources resulted in a decrease in NO_x emissions in the same boiler of from 40 to 50%. The reason for these dramatic reductions has not yet been determined but there is considerable evidence to believe that the nitrogen content of the fuel may be responsible. In any event, even a switch within a given type fuel can potentially effect a reduction in emissions.

Fuel availability and price structure in the U.S. is very complex. There are many factors involved in determining the ultimate availability and price. In a given location fuel prices and availability can vary widely depending on geographical considerations, user category, quantities consumed, etc. Although substitution with lower NO_x producing fuel potentially offers some help for the NO_x problem, widespread substitutions undoubtedly would have an adverse effect on the entire fuel supply structure and ultimately could limit the availability of the lower NO_x producing fuels.

7.2. NUCLEAR GENERATION

The substitution of nuclear generation for fossil fuel generation is a very effective means of limiting urban population exposure to NO_x emissions. Since actual experience with large nuclear power generating stations is relatively limited, it is difficult to predict accurately future nuclear generation. Published forecasts of nuclear generating capacity for the year 1980 for the last few years showed an increasing trend as follows: July, 1963 - 40,000 megawatts (7-3); FPC's Natural Power Survey of October 1964 - 70,000 MW (7-4); AEC on February, 1967 - 80 to 110,000 MW; and AEC on May, 1967 - 120 to 170,000 MW. However, construction delays (7-5), (7-6), (7-7) rapidly increasing costs, difficulties in finding suitable, approved plant sites and other problems have raised doubts that the industry can achieve more than 110,000 Megawatts capacity by the year 1980. As illustrated in Section 9.3, the use of nuclear generation is the most important method planned for future reduction of NO_x emissions in the Chicago region. For the entire United States, the substitution of nuclear generation for fossil fuel generation is expected to reduce NO_x emission by 3.6 million tons in 1980.

7.3. REMOTE PLANT LOCATION

Mine mouth generation, including midrange generating sites offering the advantages of inexpensive fuel, ample water supply, favorable transmission distances and remoteness from population centers is another significant trend affecting pollution. Of the 65 major thermal units of 500 megawatt capacity or larger scheduled for completion before 1972, twenty-nine units at 19 locations or 45%, will be at sites classified either as mine mouth or midrange* (7-3). The Federal Power Commission's National Power Survey (7-4) published in December 1964, estimated that by 1980 mine mouth generation would constitute about 17% of total U.S. capacity.

Similar considerations apply, in principle, to the prevention of urban population exposure to NO_x emissions from other intense, localized sources, such as plants manufacturing or using nitric acid. However, the supply of raw materials, the availability of utilities, and the distribution and sales of products make this approach subject to a case-by-case type of evaluation.

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* During the same period 30 nuclear units of 300 megawatt capacity or larger are scheduled for completion.

TABLE 7-1

COMPARISON OF NO_x EMISSIONS BETWEEN GAS, OIL AND COAL ON AN EQUIVALENT BTU BASIS (7-1)

Fuel	Average NO_x Emissions (Pounds $NO_x/10^9$ BTU) Household and Commercial	Industry	Electric Generation
Natural Gas (1046 BTU/Cu Ft) (7-2)	111	205	373
Fuel Oil (149,966 BTU/Gal) (7-2)	80-480	480	693
Coal (11,867 BTU/Pound) (7-2)	337	842	842

7.4. NON-CONVENTIONAL POWER GENERATING CYCLES

Most of today's fossil fueled power plants use the conventional Rankine steam cycle for generating power. The use of higher steam temperatures, the advent of the steam reheat and superheat cycles, regenerative feedwater heating, and improved design of furnaces, boilers and turbines have all increased plant efficiency. The advent of the supercritical steam cycle has provided a more recent route to improved power generation. Future improvement will probably come from the use of improved materials of construction and generating cycles. Advanced thermal cycles that are likely to offer future improvements are:

- The multivapor topping and bottoming cycle.
- The exhaust fired combined cycle.
- The supercharged boiler-combined cycle.
- The closed cycle gas turbine.
- The magnetohydrodynamic cycle.

Other "exotic" power generating cycles such as fuel cells, thermionic and thermoelectric generators, etc., are so far removed from practical application to central power generation, that their potential impact on the stationary NO_x problem up to the year 2,000 is considered to be insignificant.

A multivapor cycle combines the use of steam with either or both a higher temperature boiling fluid (topping cycle) and a lower temperature boiling fluid (bottoming cycle). This permits adding and rejecting more heat over a wider range of temperature than is possible with a single fluid and thereby results in increased thermal efficiency. Mercury was tried as a topping fluid by Public Service Electric and Gas Co. but operating problems caused its shutdown. Ammonia and freon have been proposed for bottoming cycles and the former was evaluated and found to be potentially attractive in a study carried out at the Franklin Institute Research Laboratories for the U.S. Department of Interior's Office of Coal Research (7-8).

In the exhaust fired combined cycle, a clean fuel is added to the exhaust from a lean-fired gas turbine (i.e., O_2 available in turbine exhaust) and this hot exhaust-fuel mixture combusted in a steam boiler. The total power derived from the gas and the steam turbines in such a cycle could be about 5% more than that from the straight steam cycle.

In the supercharged boiler-combined cycle, the furnace of a steam generator is operated under pressure. Rather than cool-down the combustion gases as much as possible against steam raising surface before discharge, the gases are taken down to only about 1600°F and then exhausted through a gas turbine. The supercharged boiler may also be run under substoichiometric air/fuel conditions, with air added upstream of the gas turbine to form a two-stage combustion process. Thermal efficiency for the supercharged boiler-combined cycle might be 6-8% more than that obtained in the conventional Rankine cycle.

The closed-gas turbine cycle exhausts compressed gas, preheated indirectly to high temperatures (~2000°F) in a furnace, through a turbine. The working fluid, an inert gas, is recompressed and is then preheated by the gas turbine exhaust. Increases in thermal efficiency in excess of 10% are approachable in this cycle by exhausting the furnace gas through a steam boiler.

In the magnetohydrodynamics cycle (MHD), a very high temperature ionized combustion gas is exhausted through a magnetic field to generate a current directly in the gas. Electrodes in the gas stream are used to withdraw this current. Exhaust gas temperatures up near 5000°F are needed for this system and the gas is usually seeded with some material such as an alkali metal to make it ionize more readily. A MHD generator exhausting into a conventional steam plant can provide very high thermal efficiencies-perhaps 25 to 30% higher than a conventional steam cycle.

Ordinary fuels with conventional air preheat temperatures will not provide the high temperatures required by this cycle. Therefore, combinations of oxygen enrichment, higher air preheat temperatures and supercharged combustion must be used and these all promote NO formation. In a paper study on MHD, Hals and Jackson (7-9) estimated that NO concentrations approaching equilibrium values of 1 to 1.5% could be achieved. They suggest that economic recovery of the NO would be possible at these concentrations and indeed some of the flue gas emission control processes outlined in Section 5 of the report could be attractive under these circumstances. Without such control, NO_x emissions would be about ten times those of conventional power plants.

Based on differences in these cycles, changes in nitrogen oxide emissions are to be expected. Table 7-2 shows the expected direction of these changes. It has been developed considering a number of different factors. To begin with, increased cycle efficiency will result in lower fuel consumptions. All other things being equal, this will reduce nitric oxide emissions. Higher combustion temperatures, however, produce more nitrogen oxides per pound of fuel burned. A higher temperature might result from increased combustion intensity (i.e., heat release rate per unit volume) resulting from pressurized or enriched air combustions (i.e., supercharged boiler). Fuel rich combustion, on the other hand, would produce less nitrogen oxides since less oxygen would be available for combination with nitrogen. Two-stage combustion also appears to decrease nitric oxide formation. Gas turbines, while producing lower nitric oxide effluent concentrations than do furnaces, use several times their stoichiometric air requirements and on a lbs NO_x/BTU basis, there may be little difference between them.

Table 7-2

NO_x Pollution Potential of Advanced Power Cycles

Cycle	Change Expected Relative to Conventional Steam Cycle NO_x (Lbs/KWH)
Vapor Topping and Bottoming Cycle	Decrease
Exhaust-Fired Combined Cycle	Decrease
Supercharged-Boiler Combined Cycle	Increase
Supercharged-Gasifier Combined Cycle	Decrease
Closed-Cycle Gas Turbine	Decrease
Magnetohydrodynamic Cycle	Very Large Increase Without Flue Gas Control

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8. COST ESTIMATES FOR EXISTING AND POTENTIAL NO_x CONTROL METHODS

In this section, control costs are developed for the existing and potential NO_x control methods discussed in Sections 4, 5 and 6.

8.1. COMBUSTION MODIFICATION METHODS

Cost estimates have been made for the combustion modification NO_x control techniques assessed to be technically attractive in Section 4. These techniques are low excess air firing, 2-stage combustion, flue gas recirculation, steam or water injection, and combinations of these techniques.

8.1.1 Low Excess Air Firing

Cost estimates for low excess air operation in public utility boilers were made on the basis of the necessity of modifying the burner windbox to add division plates and isolating dampers so that the air to each burner may be individually controlled. As noted in Table 8-1, direct estimates were made for oil and gas firing only, since detailed requirements to achieve low excess air firing in a pulverized coal system have not yet been developed. Recognizing the difficulties which may prevail in achieving this type of operation with pulverized coal, cost estimates for this fuel, for the purposes of this report, were then taken as 150% of those for gas or oil. Division plates and isolating dampers will also be required for pulverized coal firing but, in addition, some means must be provided to insure uniform distribution of the coal to all burners, particularly those served by a single pulverizer. It is assumed that the 50% increase included in the estimate will cover these additional costs.

Low excess air operation in many ways is more exacting with regard to combustion control requirements than operation at higher excess air levels with "built in" cushions by virtue of the greater amount of excess air present. Existing combustion control systems of good quality no doubt will be able to accomodate operation at low excess air with little difficulty. However, to be conservative, an additional investment factor has been included in the cost estimates to provide improvements in the combustion control system if required for low excess air operation. Again, the problem of obtaining uniform fuel distribution in a pulverized coal system may require additional controls. These controls have been included in the allocation for coal system costs.

Many oil fired public utility boilers in Europe and a considerable number of oil and gas fired boilers in the U.S. have been converted (or more properly, re-adjusted) successfully to low excess air operation without incurring costs for modifications or additional controls. Most of these conversions were made to eliminate costly and troublesome operating problems such as slagging, air heater plugging and high and low temperature corrosion conditions in oil fired boilers. Low excess air operation with gas has been practiced mainly in West Coast power plants to reduce NO_x emissions. In addition to these important operating benefits, other major operating savings have accrued. Some operators have reported (4-40, 8-1) increases in efficiency from 0.5 to as high as 2 percent as a result of low excess air firing. In this study, decreased operating costs for oil, gas and coal were calculated as equivalent to a 1% savings in fuel costs. In public utility boilers an additional 1% savings was included to account for decreased maintenance and operating costs resulting from elimination of corrosion and slagging problems in oil fired boilers. Since oil fired industrial and commercial boilers are not plagued to the same extent by these problems, these additional savings were not included in cost estimates for the latter type of equipment.

In considering low excess air operation for control of NO_x emissions in industrial and commercial boilers, it was concluded that the benefits of this type of control could be achieved without alterations or modifications to the firing equipment. This is reflected in the zero equipment investment cost indicated in Table 8-2. The larger number of boilers in existence are under 100,000 pounds of steam per hour in size and generally are fired by one burner. The average excess air used in these boilers is about 25% with some operating as high as perhaps 40 percent. It was concluded, after discussions with experts in the field, that decreases in excess air to about 5%, or sufficient to obtain the desired NO_x reductions, would be possible on most units without resorting to major burner redesign. Since most present day industrial or commercial boilers are factory assembled with complete automatic control systems, a similar allowance to add combustion control instrumentations for low excess air operation has been included in the estimates for this type equipment as for public utility boilers.

Most industrial and commercial boilers today are of the factory assembled, fully automated type, many of them unattended. Reliable, trouble free, automatic operation is a major attraction of these units. In many cases, owners depend heavily on factory service engineers for inspection, burner cleaning and adjustments, annual boiler cleaning, etc. to keep their boilers in reliable operating condition. Reducing excess air on boilers of this type could tend to make automatic operation more critical. Cost estimates, therefore, included allowances for additional service by factory or dealer representatives to assure trouble-free operation. Present procedure was assumed to consist of one burner cleaning and adjustment and one boiler cleaning per year at $125 annually. Operating costs included in the estimates for low excess air operation on boilers under 40,000 pounds of steam per hour were increased by $425 to include quarterly burner cleaning and adjustment, semi-annual boiler cleaning, and 8 burner inspections. Service charges on larger boilers provided for incremental service charges of $700 annually to allow for more expensive cleaning costs in the bigger units.

Low excess air firing of existing refinery furnaces is not recommended. Heat transfer rates and distribution are very sensitive in a refinery furnace to avoid hot spots, coking inside of furnaces tubes, and corrosion of tube hangers. Most furnaces are of natural draft design with the air rate controlled by damper setting. Furthermore, many furnaces burn by-product gas or liquid fuels of fluctuating compositon and heat content. Thus, inadequate control of air rate and fluctuating fuel quality limit reductions in excess air.

8.1.2. Two Stage Combustion

Cost estimates of NO_x control by modifications for 2-stage combustion envision increasing the size of the windbox in public utility boilers, installation of separate air ports above the top row of burners, and connecting ducts from the windbox to each port with a separate control damper in each duct. Estimates for a 100 and 750 MW unit are given in Table 8-1. Costs for other sizes may be obtained by reference to Figure 8-1. As noted in Section 4, 2-stage combustion has been found to be an effective means for reducing NO_x emissions in oil and gas fired boilers. The technique has not yet been proven in commercial units firing pulverized coal. Cost estimates in this report, however have assumed that the technique will eventually be adapted to P.C. firing. Since the principles are the same regardless of the fuel fired, modification costs are also assumed to be the same with any type of firing.

Cost estimates for two-stage combustion modification in this report were made on two separate bases. First, as discussed above, estimates were made of capital expenditures required to alter or redesign equipment to incorporate two-stage combustion operating principles. Second, additional cases were considered based on the Pacific Gas & Electric Company's experience where the effect was achieved through simulated operation at no cost for alteration or redesign of equipment. As mentioned in Section 4.4.1.2., remarkable reductions in NO_x emissions (from 1500 ppm to about 200 ppm on two 750 MW boilers) were achieved by PG&EC on the gas fired boilers at their Moss Landing Station by a simulated or modified form of two-stage combustion in combination with low excess air operation. Two-stage combustion was simulated by cutting the fuel off in the top burners, burning the fuel in the remaining bottom burners under sub-stoichiometric conditions, and using the top burners as air ports to supply air for burnout. Demonstration tests will be required on boilers of various sizes and design types to assess the applicability of this approach. Thus, estimates for two-stage combustion in this report were made on the basis of either zero capital investment costs for the modified form of two-stage combustion or full charges for complete alteration or redesign of equipment.

Tangential firing as discussed in Section 4.4. has been observed to give reduced NO emissions in utility boilers. Tangential firing, as such, is a combustion method of specific design, rather than a combustion modification technique for NO_x control. Based on the available information, tangential firing and two-stage combustion produce comparable reduction in NO_x emissions. Furthermore, from the cost standpoint, tangential firing and opposed wall and front wall firing with two-stage combustion are competitive. Also, both of the above methods of firing utilize the principle of spreading out the flame envelope through more of the furnace volume which results in lower effective flame temperatures, and hence in lower NO_x emissions. Therefore, the combustion modification techniques and their combinations already discussed in Section 4.4., are deemed potentially applicable to both of these firing methods for NO_x control. On this basis, the cost and cost-effectiveness analyses (which are to follow in Section 9) developed for two-stage combustion techniques are also indicative of factors which may be applied to tangential firing.

Two-stage combustion as a means of NO_x control in industrial or commercial boilers is presently considered uneconomical for the overwhelming majority of this type of equipment. Most boilers in this classification are very small with relatively restricted furnace or combustion chamber confines. In addition these units are normally factory assembled to designs which do not lend themselves to easy or economic modification. NO_x emission rates in these boilers are also relatively low. Technically, two-stage combustion undoubtedly would achieve a decrease in NO_x emissions in these applications. However, considering the great numbers of small boilers of this type in existence with small fireboxes not readily adaptable to 2-stage operation and the expense of making alterations, further study of potential convertibility is recommended for later phases of this effort.

Control of NO_x emissions by 2-stage combustion is not viewed as being practical in refinery furnaces. As noted above, excellent combustion conditions must prevail in furnaces of this type to achieve precise heat transfer to prevent coking inside furnace tubes, hot spots, hanger corrosion, etc. Two-stage combustion produces long smoky flames which can impinge on furnace tubes and upset effective heat transfer. For these reasons, no estimates were made for 2-stage combustion control in this type of equipment.

8.1.3 Flue Gas Recirculation

Estimated costs of adding flue gas recirculating equipment to a given process includes the cost of the recirculating fan and duct work sized to recirculate the necessary volume of combustion flue gases at the proper temperature and pressure from a point near the gas exit back to the burner windbox. Injection of the gases into the furnace would be through the individual burners in order to achieve the greatest effect on NO_x emissions. Cost estimates would include the necessary fan drivers and controls. For public utility boilers the recirculating system would be sized for recirculating a maximum of 15% of the flue gases. Greater quantities, especially in combination with low excess air operation, would tend to dilute the combustion air too much and possibly affect the stability of the flame. Investment cost estimates for flue gas recirculation are listed in Table 8-1 for 100 and 750 megawatt public utility boilers and estimates for other sizes may be obtained from Figure 8-1. An operating cost debit of 2.4 horsepower per megawatt of installed capacity has also been included in the cost estimates for this type of control in utility boilers.

Cost estimates for flue gas recirculation applications to industrial and commercial boilers and refinery furnaces were calculated on the basis of recirculating a maximum of 30% of the flue gas. Fan horsepower consumption was debited in the cost estimates as an increase in operating costs. Estimated investment costs and fan power consumption requirements are listed for the respective equipment in Tables 8-2 and 8-3.

8.1.4 Steam or Water Injection

In this report, cost estimates were only made for water injection since it appears that raw, cold water would be more effective in reducing NO_x than steam. Water injection also involves more equipment by virtue of the need to supply a separate injection pump and attendant piping. If steam were used, its supply would be taken from a low pressure auxiliary source in the plant, requiring no further complications for its injection. Cost estimates made for water injection were made on the basis of installing separate atomizers in each individual burner together with the required piping. This equipment is in addition to the injection pump and could be used for either steam or water injection. Table 8-1 and Figure 8-1 provide investment cost data for public utility boiler installations and similar investment data for industrial and commercial boilers are given in Table 8-2. No investment cost estimates were made for refinery furnace applications since this type of control is not viewed as being practical. All cost estimates take into account additional operating costs with this control technique due to the heat lost in vaporizing the water. As previously indicated in Section 4, increased operating costs were calculated as being equivalent to 1% loss in efficiency.

8.1.5 Combinations of Combustion Modification Control Methods

When combinations of combustion modification techniques are employed in reducing NO_x emissions, the investments made in alterations for each type of control are obviously additive. This is reflected in the investment cost data listed in Tables 8-4 and 8-5. The estimated investment costs in equipment and instruments for the different NO_x combustion control methods are listed in Table 8-4 for public utility boilers. These investment data were used in further control cost calculations described later. No start-up costs are included on the assumption that any costs incurred would be absorbed in normal operating accounting. As discussed in Section 8.1.2., low excess air operation and two-stage combustion have been achieved in power plant boilers without incurring investment costs for alterations or redesign, especially in the larger sized units. It was assumed in Table 8-4, therefore, that all of the 1000 MW gas and oil fired boilers would be in this classification, incurring no costs for making the conversions. However, it was also estimated that 10% of the 750 MW, 25% of the 500 MW, 50% of the 250 MW and 90% of the 120 MW would require investments, the remainder being converted at no cost. In addition, since this type of operation has not yet been proven in pulverized coal fired boilers, it was considered that investments would be required in all of the P.C. fired units. This is reflected in Table 8-4 by taking the respective percentages mentioned of the estimated capital equipment investment costs.

8.1.6. Combustion Modification Costs

Table 8-1 lists the capital cost factors used for cost estimating the different combustion modification techniques discussed for NO_x emissions control on utility boilers.

Table 8-1

Public Utility Boilers

Combustion Modifications for NO_x Control
Investment Cost Factors, $/KW (Delivered and Erected)

	750 Megawatt		100 Megawatt	
Modifications	Oil & Gas	Pulv. Coal	Oil % Gas	Pulv. Coal
Low Excess Air	0.25	*	0.363	*
Flue Gas Recirc.	0.656	0.656	1.033	1.033
2-Stage Combustion	2.08	2.08	3.30	3.30
Steam or Water Injection	0.0238	0.0238	0.0363	0.0363

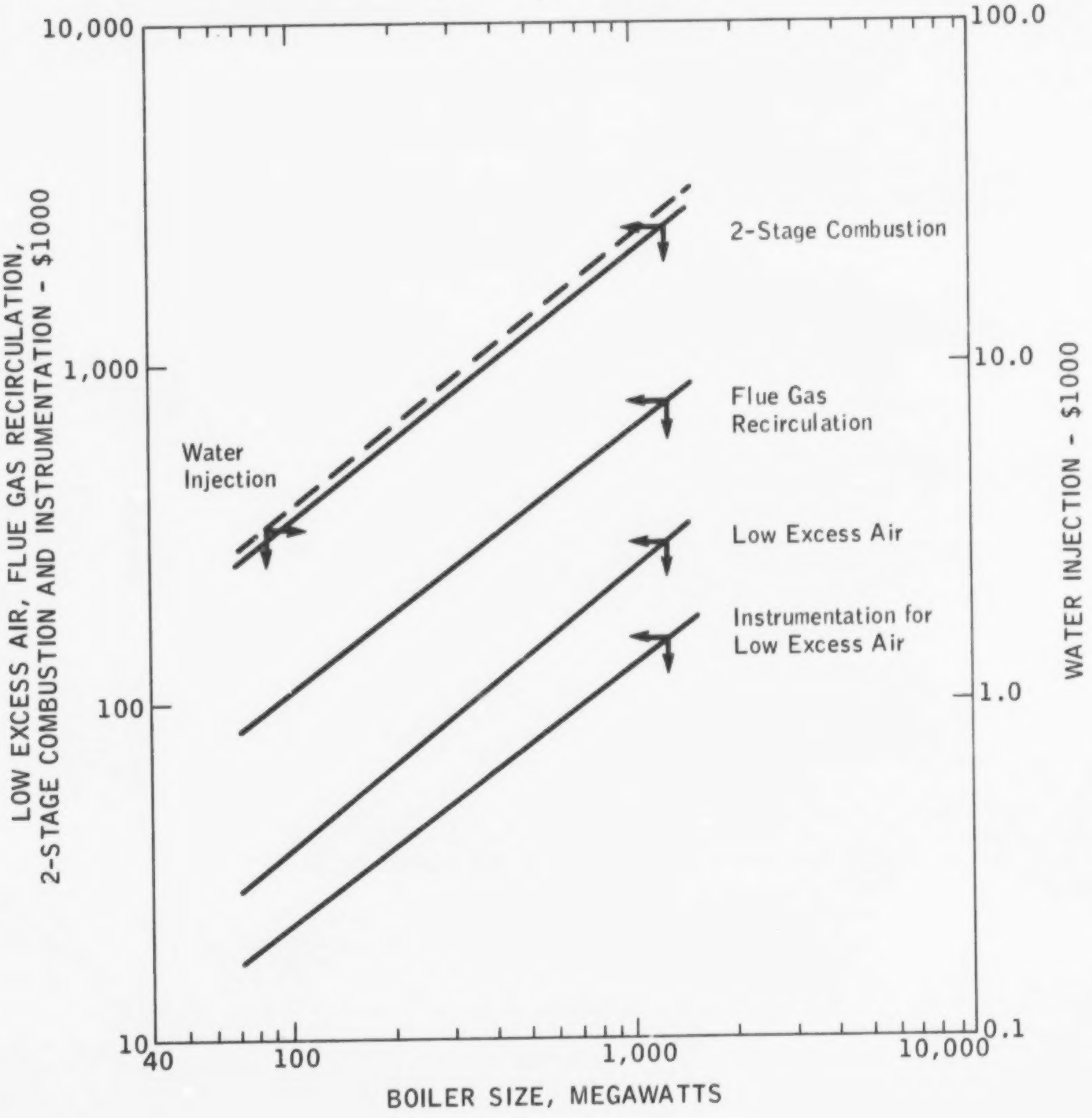
* Hypothetical Case - assumed cost 150% that for oil and gas.

These cost factors were developed in consultation with the Babcock and Wilcox Company. Factors were calculated for two different size units, 750 and 100 megawatts, and are given as additives to base costs for new units in dollars per kilowatt. Modifications for existing units can be estimated from these base data by adding an appropriate experience factor for the locality, perhaps 20 to 25%, to reflect the additional costs incurred in making the same modifications in the field. Plant investment costs established from the factors in Table 8-1 have been plotted in Figure 8-1 and used in developing Table 3-4.

Figure 8-1

PUBLIC UTILITY BOILERS

INVESTMENT COST ESTIMATES
OF COMBUSTION MODIFICATIONS
FOR NO_x CONTROL



Investment cost estimates for industrial and commercial boiler installations are provided in Table 8-2. Certain assumptions were made in considering applications of combustion modifying techniques to these units as discussed in later sections. As noted in Table 8-2, the sizes for which investment estimates were made were derived by averaging available boiler census data. The size of commercial boilers in each category available to industry would bracket these average sizes. Estimates for actual sizes could be extrapolated from the data in Table 8-2, if desired.

Table 8-2

Industrial and Commercial Boilers

Investment Costs Estimates of Combustion Modifications for NO_x Control

	Low Excess Air		Flue Gas Recirculation		Water Injection
Watertube Boilers	Equip. Inv. $	Instr. Inv. $	Equip. Inv. $	Horse Power*	Equip. Inv. $
#Steam/Hr. **					
27,700	0	3,000	8,000	49	1,800
36,100	0	3,250	14,000	55	2,000
144,500	0	6,500	100,000	89	2,700
187,500	0	7,500	133,000	115	3,000
Firetube Boilers					
#Steam/Hr.					
3,690 (107 BHP)	0	2,000	2,500	6	1,000

* Net horsepower consumed (basis for operating costs)

** Average sizes derived from boiler census data (not to be construed with commercial size ratings)

Table 8-5 lists the investment and start-up costs used in calculations of combustion modification control costs for industrial and commercial boilers. For purposes of this report it was assumed that the required start-up service would be furnished by factory or dealer representatives and charged to the owner's account. Since these costs are relatively large in comparison to overall operating costs, their inclusion as a part of the charges against NO_x control in these boilers is justified.

Cost estimates for refinery furnaces were made on recent designs of a small and large furnace, and are tabulated in Table 8-3. Input rates of 50 million and 300 million BTU/hr, respectively, were selected as being representative of the sizes presently found in refineries. Estimates for other sizes may be extrapolated from these data. As amplified in later paragraphs, cost estimates were made only for flue gas recirculation control; other controls not being suitable to this equipment, as discussed in Section 4.

Table 8-3

Refinery Furnaces

Investment Cost Estimates of Recirculating Flue Gas For NO_x Control

Furnace Size (Heat absorbed)	50 MM BTU/Hr	300 MM BTU/Hr
Furnace Type	Vertical Cylindrical	Cabin
Investment		
No Recirculation		
Material	$133,900	$712,500
Labor	27,000	152,700
Total	$160,900	$865,200
30% Recirculation		
Material	$151,100	$867,000
Labor	29,900	180,000
Total	$181,000	$1,047,000
Increased Operating Cost for 30% Recirculation		
Horsepower Requirement		
Installed	89 hp	530 hp
Operating	63 hp	386 hp

Basis of Estimates: All costs are 2nd quarter '69 at standard location. Only furnace equipment costs (including blowers) are reflected in above costs. Non-equipment costs (i.e. foundations, site preparation, instrumentation, feed piping) and contractor's field labor overheads and fees are not included.

TABLE 8-4

PUBLIC UTILITY BOILERS - 1980

Investment Costs, 1000's Dollars

Plant Size Fuel	Low Excess Air Investment			Two Stage	LEA + 2-Stage	Flue Gas Recirc.	LEA + Recirc.	Water Injection
	Equip.	Instr.	Total					
1000 MW								
Gas	0*	120	120	0*	120	600	720	23
Oil	0*	120	120	0*	120	600	720	23
Coal	360**	120	480	1,900**	2,380	600	1,080	23
750 MW								
Gas	19*	100	119	153*	272	490	609	19
Oil	19*	100	119	153*	272	490	609	19
Coal	285**	100	385	1,530**	1,915	490	875	19
500 MW								
Gas	34*	72	106	280*	386	360	466	14
Oil	34*	72	106	280*	386	360	466	14
Coal	203**	72	275	1,120**	1,395	360	635	14
250 MW								
Gas	39*	43	82	330*	412	210	292	8
Oil	39*	43	82	330*	412	210	292	8
Coal	116**	43	159	660**	819	210	369	8
120 MW								
Gas	38*	25	63	342*	405	120	183	5
Oil	38*	25	63	342*	405	120	183	5
Coal	63**	25	88	380**	468	120	208	5

* Investment required to modify zero % of 1000 MW; 10% of 750 MW; 25% of 500 MW; 50% of 250 MW; and 90% of 120 MW oil and gas fired boilers.

** All coal fired boilers require investment for modification.

TABLE 8-5

INDUSTRIAL AND COMMERCIAL BOILERS - 1980

Type of Firing	Boiler Size # STM/Hr	Investment and Start-Up Costs, 1000's of Dollars							
		Low Excess Air		Flue Gas Recirc.		LEA + Recirc.		Water Inject.	
		Start Up	Instr.	Start Up	Inv.	Start Up	Inv.	Start Up	Inv.
Watertube Boilers									
Gas	27,700	.6	3.0	.6	8.0	1.2	11.0	.2	1.8
Oil	27,700	.6	3.0	.6	8.0	1.2	11.0	.2	1.8
Gas	144,500	.6	6.5	.6	100.0	1.2	106.5	.2	2.7
Oil	144,500	.6	6.5	.6	100.0	1.2	106.5	.2	2.7
Coal	36,100	.6	3.25	.6	14.0	1.2	17.25	.2	2.0
Coal	187,500	.6	7.5	.6	133.0	1.2	140.5	.2	3.0
Firetube Boilers									
Gas	107*	.6	2.0	.6	2.5	1.2	4.5	.2	1.0
Oil	107*	.6	2.0	.6	2.5	1.2	4.5	.2	1.0

* In boiler horsepower.

The estimated investment and start-up cost data developed were used to form the basis for further calculations of combustion modification control costs. These data are tabulated in columns (1) and (2) on the calculation sheets for start-up and capital equipment costs, respectively. Table 8-6, Sample Calculations, illustrates the type of calculations which are made on the basic investment cost estimates. Examples of the results of actual calculations are provided in Tables 8-7, 8-8, 8-9 and 8-10. Detailed calculations using this methodology are given in Appendices 8-1 through 8-20. Referring to Table 8-6 column (3), it will be noted that annual capital charges are charged off at the rate of 14% in line with NAPCA's guidelines. Since 50 percent of the start-up costs are tax deductable under normal corporate rates, only half of the charges in column (1) are added to the capital equipment charges, column (2), before applying the 14% annual fixed charge rate.

In column (4), Table 8-6, maintenance is charged off as a percentage of the annual capital charges, column (3). The rate at which maintenance is applied varies in accordance with guideline experience factors for the particular service classification. Supplies are charged at 15% of maintenance and overhead is taken at 50% of maintenance plus supplies, in accordance with experience in these installations. Thus, operating charges for maintenance, supplies and overhead used in column (4) for instruments at 10% of annual capital charges; modifications having moving parts such as fans and dampers charged at 5% and alterations having no moving parts charged at 1% are:

Instruments

Maintenance = 10% = 0.10
Supplies = .10 x 1.15 = 0.115
Overhead = 0.115 x 1.50 = 0.1725

Modifications Having Moving Parts

Maintenance = 5% = 0.05
Supplies = .05 x 1.15 = 0.0575
Overhead = .0575 x 1.5 = 0.0863

Modifications Having No Moving Parts

Maintenance = 1% = .01
Supplies = .01 x 1.15 = .0115
Overhead = .0115 x 1.5 = .0173

Since modifications for low excess air operation require investments in both instruments and capital equipment, dual charges are made on these items at the proper rates as indicated in column (4) Table 8-6. Modifications for 2-stage combustion having no moving parts are charged at the 0.0173 rate. Equipment used in flue gas recirculation and water injection such as fans and pumps are charged at the intermediate, moving parts rate of 0.0863.

TABLE 8-6

SAMPLE CALCULATIONS

COMBUSTION MODIFICATION CONTROL COSTS

Plant Size ______________

Fuel ________
____

Annual Operating Hours ________
____

	Fixed Costs			Operating Costs		
Control Method	Start-Up Costs $1000	Capital Equipment Costs $1000	Annual Capital Charges $1000	Maintenance Supplies and Overhead $1000	Other Operating Costs $1000	Total Costs Per Year $1000
	(1)	(2)	(3)	(4)	(5)	(6)
I. Low Excess Air		Equip. Inv. = A Instr. Inv. = B A+B	$.14\left[\frac{(1)}{2} + (2)_{A+B}\right]$	.0863 x (2)A + .173 x (2)B		(3)+(4)+(5)
II. 2-Stage Combustion			$.14\left[\frac{(1)}{2} + (2)\right]$	.0173 x (2)	0	(3)+(4)+(5)
III. Low Excess Air + 2-Stage Comb.	I + II	I + II	$.14\left[\frac{(1)}{2} + (2)\right]$	I + II	I + II	(3)+(4)+(5)
IV. Flue Gas Recirculation			$.14\left[\frac{(1)}{2} + (2)\right]$	.0863 x (2)		(3)+(4)+(5)
V. Low Excess Air + Flue Gas Recirc.	I + IV	I + IV	$.14\left[\frac{(1)}{2} + (2)\right]$	I + IV	I + IV	(3)+(4)+(5)
VI. Water Injection			$.14\left[\frac{(1)}{2} + (2)\right]$	.0863 x (2)		(3)+(4)+(5)

TABLE 8-7

PUBLIC UTILITY BOILERS

Combustion Modification Control Cost

Boiler Size 1000 MW Fuel Gas Load Factor 6120 Hrs/Hr

Control Method	Fixed Costs			Operating Costs		
	Start-Up Costs $1000 (1)	Capital Eq Costs $1000 (2)	Capital Charges $1000 (3)	Maint., Suppl. and Overhead $1000 (4)	Other Oper. Costs $1000 (5)	Total Cost Per Year $1000 (6)
Low Excess Air		0 120 120	17	0 21 21	(133)*	(95)
2-Stage Combustion		0	0	0	0	0
Low Excess Air + 2 Stage Comb.		120	17	21	(133)	(95)
Flue Gas Recirculation		600	84	52	66	202
Low Excess Air + Flue Gas Recirc.		720	101	73	(67)	107
Water Injection		23	3	2	133 6 139	144

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*Figures in parenthesis indicate operating savings in all cost and cost-effectiveness tables.

TABLE 8-8

PUBLIC UTILITY BOILERS

Combustion Modification Control Cost

Boiler Size 1000 MW Fuel Oil Load Factor 6120 Hrs/Yr

	Fixed Costs			Operating Costs		
Control Method	Start-Up Costs $1000 (1)	Capital Eq Costs $1000 (2)	Capital Charges $1000 (3)	Maint., Suppl. and Overhead $1000 (4)	Other Oper. Costs $1000 (5)	Total Cost Per Year $1000 (6)
Low Excess Air		0 120 120	17	0 21 21	(335)	(297)
2-Stage Combustion		0	0	0	0	0
Low Excess Air + 2 Stage Comb.		120	17	21	(335)	(297)
Flue Gas Recirculation		600	84	52	66	202
Low Excess Air + Flue Gas Recirc.		720	101	73	(269)	(95)
Water Injection		23	3	2	168 6 174	179

TABLE 8-9

PUBLIC UTILITY BOILERS

Combustion Modification Control Cost

Boiler Size 1000 MW Fuel Coal Load Factor 6120 Hrs/Yr

	Fixed Costs			Operating Costs		
Control Method	Start-Up Costs $1000 (1)	Capital Eq Costs $1000 (2)	Capital Charges $1000 (3)	Maint., Suppl. and Overhead $1000 (4)	Other Oper. Costs $1000 (5)	Total Cost Per Year $1000 (6)
Low Excess Air		360 120 480	67	31 21 52	(198)	(79)
2-Stage Combustion		1900	266	33	0	299
Low Excess Air + 2 Stage Comb.		360 120 1900 2380	333	31 21 33 85	(198)	220
Flue Gas Recirculation		600	84	52	66	202
Low Excess Air + Flue Gas Recirc.		360 120 600 1080	151	31 21 52 104	(132)	123
Water Injection		23	3	2	132 6 138	143

TABLE 8-10

INDUSTRIAL AND COMMERCIAL BOILERS

Combustion Modification Control Costs

Boiler Size 27,000 lb steam/HR Watertube   Fuel Gas / Oil   Load Factor 4280 Hrs/Yr / 4530 Hrs/Yr

	Fixed Costs			Operating Costs				
Control Method	Start Up Costs $1000 (1)	Capital Equipment Costs $1000 (2)	Capital Charges $1000 (3)	Maintenance, Supplies and Overhead $1000 (4)	Other Operating Costs $1000 (5) Gas	Other Operating Costs $1000 (5) Oil	Total Costs Per Year $1000 (6) Gas	Total Costs Per Year $1000 (6) Oil
LEA	0.6 (6 Man Days)	Equip 0 Instr 3.0	0.462	17.3% .0798	(.349)* .425** .076	(.454)* .425** (.029)	0.618	0.513
Recirculation (40 HP)	0.6 (6 Man Days)	8.0	1.16	8.63% 0.100	.765	.811	2.025	2.071
LEA + Recirc	1.2 (12 Man Days)	11.0	1.62	.1798	.841	.782	2.641	2.582
Water Injection	0.2 (2 Man Days)	1.8	.258	8.63% .022	.349	.454	.629	.734

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*Based on one percent increase in efficiency for gas, oil and coal (fuel savings)

**Based on extra service required for LEA ($425 increase for up to 36,100 lb steam/hr; $700 increase for over 36,000 lb steam/hr)

Other operating costs or debits calculated for each combustion modification control technique are tabulated in column (5) on the calculation sheets. Referring to Table 8-10, column (5), low excess air operation increases efficiency resulting in decreased fuel usage and an operating cost savings. In this instance, on the basis of 1% increase in efficiency and gas and oil at the U.S. average price of 25¢ and 32¢ per million BTU, respectively, the calculated savings are:

$$\text{Gas} = 0.01 \times 32.6 \times 10^6 \ \frac{\text{BTU}}{\text{Hr}} \times \frac{\$0.25}{10^6 \ \text{BTU}} \times 4280 \ \frac{\text{Hrs}}{\text{Yr}} = \$349/\text{Yr.}$$

$$\text{Oil} = 0.01 \times 31.3 \times 10^6 \ \frac{\text{BTU}}{\text{Hr}} \times \frac{\$0.32}{10^6 \ \text{BTU}} \times 4530 \ \frac{\text{Hrs}}{\text{Yr}} = \$454/\text{Yr.}$$

As previously indicated, savings for oil fired public utility boilers are calculated on the basis of a 2% increase in efficiency, rather than 1% to account for decreased slagging and corrosion operating costs. For coal firing, the examples in Tables 8-7, 8-8 and 8-9 are calculated on the basis of 1.5% to allow for decreased operating costs with this fuel at low excess air conditions, due to decreased low temperature corrosion.

As noted on Table 8-10, column (5), the increased service necessitated by low excess air operation is charged off as an increased operating cost. Thus the incremental service charges of $425 per year in the case of natural gas firing offset the savings in efficiency of $349 resulting in a net additional operating cost of $76 per year, against low excess air operation. In the oil case, efficiency savings slightly overbalance the additional service charges with a net savings of $29 per year.

With regard to flue gas recirculation, the cost of driving the recirculating fan increases the cost of operating the plant and is chargeable to the operation. Referring to Table 8-10, these costs are calculated as follows:

$$\text{Gas} = 40 \ \text{H.P.} \times .746 \ \frac{\text{KW}}{\text{H.P.}} \times \frac{\$.006}{\text{KW}} \times 4280 \ \frac{\text{Hours}}{\text{Year}} = \$765/\text{Year}$$

$$\text{Oil} = 40 \ \text{H.P.} \times .746 \ \frac{\text{KW}}{\text{H.P.}} \times \frac{\$.006}{\text{KW}} \times 4530 \ \frac{\text{Hours}}{\text{Year}} = \$811/\text{Year}$$

Additional operating costs due to water injection, as previously discussed, are calculated as being equivalent to a maximum loss in efficiency of 1% due to the loss of heat in vaporizing the injected water. The calculations are identical to those detailed above for savings due to increased efficiency with low excess air operation but are obviously charged off as a cost against operation.

After the annual capital charges, maintenance costs and operating debits or credits have been calculated as described above and in Sample Calculations, Table 8-6, for columns (3), (4) and (5), they are summarized in column (6). The dollar amounts in column (6) then represent the total annual costs attributable to the respective NO_x emission control technique applied to the specific equipment and these data form the cost basis for the cost-effectiveness studies described in Section 9.

Table 8-11 tabulates the total annual costs for the various NO_x combustion modification control processes calculated for the different sizes and numbers of public utility boilers expected to exist in 1980. Since not all boilers will require conversion as indicated above, the tabulation reflects the cost of only those installations on which NO_x controls are expected to be applied. Detailed cost calculations for utility boilers are given in Appendices 8-1 through 8-15. Table 8-12 tabulates similar cost data for industrial and commercial boilers. Detailed costs appear in Appendices 8-16 through 8-20. The costs tabulated assume 100% application. Obviously, it will not be practical or economical to convert every installation. The feasibility of converting these boilers due to the large numbers of small size units and their relatively high conversion costs and limited NO_x reduction effectiveness, warrants further detailed study after controlling the more economically convertible major NO_x sources.

TABLE 8-11

1980
PUBLIC UTILITY BOILERS

TOTAL ANNUAL COMBUSTION MODIFICATION CONTROL COSTS

				Annual Modification Costs* Thousands of Dollars/Year					
Boiler Size	Fuel Used	Number of Boilers in U.S.	Annuai Hours Operated	Low Excess Air	2-Stage Combustion	L.E.A. + 2-Stage	Flue Gas Recirc.	L.E.A. + F.G.R.	Water Injection
1000MW	Gas	20	6120	(-1,900)	0	(-1,900)	4,040	2,140	2,880
	Oil	9	6120	(-2,673)	0	(-2,673)	1,818	(-855)	1,611
	Coal	61	6120	(-4,819)	18,239	13,420	12,322	7,503	8,723
750MW	Gas	23	6120	(-1,564)	529	(-1,035)	3,657	2,093	2,620
	Oil	11	6120	(-2,486)	253	(-2,233)	3,223	(-737)	1,550
	Coal	71	6120	(-4,189)	17,040	12,851	11,360	7,171	8,030
500MW	Gas	27	5620	(-945)	1,188	243	2,943	1,998	1,917
	Oil	12	5620	(-1,584)	526	(-1,056)	1,308	(-276)	1,042
	Coal	81	5620	(-2,187)	14,175	11,988	8,829	6,642	5,670
250MW	Gas	40	3942	(-160)	2,120	1,960	2,360	2,200	1,160
	Oil	18	3942	(-792)	954	162	1,062	270	648
	Coal	122	3942	0	12,688	12,688	7,198	7,198	3,558
120MW	Gas	155	2190	1,550	8,370	9,920	4,650	6,200	1,395
	Oil	71	2190	(-142)	3,834	3,692	2,130	1,988	781
	Coal	474	2190	5,214	28,914	34,128	14,220	19,434	4,266

* For all boilers in the U.S. in specified size and fuel type category.

TABLE 8-12

INDUSTRIAL AND COMMERICAL BOILERS

TOTAL ANNUAL COMBUSTION MODIFICATION CONTROL COSTS

	Number of Boilers in U.S.	Boiler Size, #STM/Hr or BHP		Annual Hours Operation	Annual Modification Costs* Millions of Dollars/Yr.			
Watertube Blrs.		< 100,000	> 100,000		Low Excess Air	Flue Gas Recirc.	L.E.A. Recirc.	Water Injection
Gas	23,950	27,700		4,280	14.8	48.5	63.3	14.88
	2,365		144,500	4,330	(-0.0556)	40.2	40.1	4.8
Oil	7,000	27,700		4,530	3.59	14.5	18.09	5.14
	692		144,500	4,510	(-0.376)	11.8	11.43	1.94
Coal	5,400	36,100		4,550	2.96	17.8	20.76	4.2
	534		187,500	4,560	(-0.0695)	12.07	12.0	1.54
Firetube Blrs.								
Cas	197,300	107**		2,320	153.0	96.0	249	38.2
Oil	203,500	107**		2,440	156.5	100.0	256.5	40.9

* For all boilers in the U.S. in specified size and fuel type category.

** In boiler horsepower.

8.2 COMBUSTION FLUE GAS TREATMENT METHODS

In Section 5 of this report, potential processes for removing nitrogen oxides from combustion flue gas were discussed as alternatives to combustion modification techniques of emission control. A number of proposed flue gas treating processes were judged to be sufficiently interesting to merit further analysis on a cost basis. Included in this category were alkaline and sulfuric acid scrubbing processes incorporating NO_2 recycle; selective catalytic reduction using NH_3, H_2S, and H_2 reductants; and catalytic decomposition. Catalytic decomposition was included in the analysis in order to determine if there was any incentive for research on this potentially simple and low capital cost control technique, even though the prospects of finding an acceptable catalyst are considered dim.

Detailed process design and cost estimates were made for 1000 MW coal, oil and gas fired power plants. Gross composition of the flue gases were assumed to be approximately those shown in Table 5.1. Average nitric oxide emissions were taken to be those shown in Table 9.16 for coal, oil and gas fired plants. Sulfur contents of the fuel were assumed to be 3% for coal and 2.5% for oil. An average load factor of 6,120 hrs/year was assumed.

In all control cases, including those involving gas fired power plants, it was assumed that the flue gas would have to be discharged to the stack at 250°F to provide about the same plume color and buoyancy as untreated gas. Where this required gas reheat, direct reheat was assumed. In this method, the hot gases produced by burning a clean fuel are mixed with the treated flue gas. Direct reheat has a lower investment cost than do other methods, but overall costs are higher (8-3). Consequently, the overall costs developed may be somewhat on the high side for all the flue gas control processes evaluated. However, their relative ranking will not be affected.

The first step in evaluating the selected flue gas emission control processes was the preparation of process flow sheets. Process conditions were specified and material, heat and energy balances were made. The various pieces of equipment were then sized and materials of construction selected.

Equipment costs were obtained with the aid of a computer system developed by Esso Research and Engineering Company for cost estimating processes for which there is a minimum of information. Esso's system contains a library of actual cost data for typical equipment used in the chemical and petroleum industry. The program automatically assigns to the specified major pieces of equipment, their usual complement of piping, valving, controls, foundations, utilities, etc. and their costs are included in the materials and labor (M + L) costs generated by the computer for the major pieces of equipment. In a few cases, where specified equipment sizes were outside the range of the computer data, extrapolations were made or actual cost quotations obtained from vendors.

The computer program was also used to estimate engineering and contractors fees, labor overhead and field burden costs associated with field erection. A 15% contingency was then added to all costs to account for equipment which is usually overlooked in the preparation of first-generation flow sheets. Working capital for the plant (spare parts, chemicals, etc.) was assessed at 6% of the direct material and labor costs and included in the total investment. The net investment for NO_x emission control was obtained from this total by subtracting an investment credit in those cases where the use of a gas scrubber eliminated the need for an electrostatic precipitator to remove fly ash. Table 8-13 shows the format used for the preparation of the individual process investment sheets.

TABLE 8-13

EMISSION CONTROL INVESTMENTS

		Obtained From
1.	Direct M + L Costs for Individual Pieces of Equipment	Computer Program
2.	M + L Sub-Total Costs	Sum of Individual 1 Costs
3.	Field Labor Overhead and Burden	Computer Program
4.	Engineering and Contractors' Fees	
5.	Sub-Total for Contingency	2 + 3 + 4
6.	Contingency	15% of 5
7.	Working Capital	6% of 2
8.	Total Plant Investment	5 + 6 + 7
9.	Investment Credit if any	
10.	Net Investment	8 - 9

A capital charge of 14% of net investment was used in computing annual operating costs. This is lower than the capital charges used by the chemical industry and assumes that the added costs of flue gas processing for emission control can be carried by utility type financing. Table 8-14 shows the other cost items used to obtain the total operating costs and the assumptions made in their calculations.

TABLE 8-14

ANNUAL CONTROL COSTS

		Charged At
1.	Capital Charges	14% of Net Investment
2.	Maintenance	5% of Net Investment
3.	Supplies	15% of 2
4.	Direct Labor	\$3/man/hr
5.	Supervision	15% of 4
6.	Payroll Burden	20% of (4 + 5)
7.	Plant Overhead	50% of (2 + 3 + 4 + 5)
8.	Utilities	
	Electricity	\$.006/KWH
	Steam	$\$.50/10^6$ BTU
	Process Water	$\$.10/10^3$ gal.
	Cooling Water	$\$.02/10^3$ gal.
9.	Fuels	See Table 8-15 for Bases
10.	Chemicals	
11.	Catalysts	

Total Costs = Sum of 1 through 11
Total Credict - See Table 8-16

Total Annual Operating Costs = Total Costs - Total Credits

$$\$/\text{Ton NO}_x\text{ Removed} = \frac{\text{Total Annual Operating Costs}}{\text{Tons NO}_x\text{ Removed (Calculated as NO}_2\text{)}}$$

Assumed fuel, chemical, catalyst and sorbent costs are shown in Table 8-15. The standard product credits that we have assumed in developing control costs for use in the cost effectiveness computations are shown in Table 8-16. These standard credits are based on the current market outlook for the various by-products. Actual by-product credits will depend on many factors including product quality, supply and demand, and transportation and marketing costs. Although detailed price and supply-demand projections were beyond the scope of this study, the sensitivity of emission control costs to variations in by-product credits has been computed and is given in this section of the report. As far as supply and demand are concerned, it is clear from Table 8-16 that individual power plants can supply only a small fraction of total demand for any one of the by-products produced.

Table 8-16 also lists the credits assumed for desulfurizing the flue gas, power savings for eliminating the electrostatic precipitator, and maintenance savings for reducing SO_3 corrosion. Of these, the desulfurization credit is the largest, and most significantly effects the final cost. The desulfurization credit shown assumes that SO_2 emissions must somehow be controlled, even in the absence of NO_x control, and that the use of either low sulfur coal or oil, or of an added flue gas desulfurization process would in the absence of NO_x control add a cost equivalent to \$.50/ton of coal or \$.125/bbl oil burned in the power plant. With the present state of desulfurization technology and the present availability of low sulfur fuels, these credits are probably too low. A higher assumed desulfurization credit would lower the incremental cost of NO_x control and could make marginal processes attractive, but "breakthrough" low cost desulfurization would make the incremental cost of NO_x removal correspondingly higher.

Tons of NO_x removed, calculated at NO_2, were obtained by multiplying the uncontrolled annual emissions estimated in Table 9-16 by the estimated percent control.

TABLE 8-15

ASSUMED FUEL, CHEMICAL, CATALYST AND SORBENT COSTS FOR ECONOMIC ANALYSIS

	Delivered Costs
Fuels	$\$/10^6$ BTU
Coal	0.25
Residual Fuel Oil	0.32
Natural Gas (at a gas burning plant)	0.25
Natural Gas (at a coal or oil burning plant)	0.40
Chemicals	\$/Ton
Limestone - 95% CaO	2.05
Mg $(OH)_2$ - Brucite	35.00
H_2SO_4 - 98%	18.00
NH_3	32.00
H_2	0.40/1000 SCF
Catalyst & Adsorbent Costs	\$/Ton
Molecular Sieve	1000
Alumina	200
Char	80
Vanadium Oxide Catalyst	$50/ft^3$

TABLE 8-16

ASSUMED STANDARD PRODUCTS AND OPERATING CREDITS FOR ECONOMIC ANALYSIS

By-Products	\$/Ton Credit Net Back to Plant	1969 U.S. Demand in 10^6 Short Tons(1)	Maximum % of U.S. Demand That a Single 1000 MW Power Plant Can Meet
Sulfur	25	9.6	0.5
H_2SO_4 - 98%	14(1)	28.7	0.6
H_2SO_4 - 80%	8(1)		
HNO_3 - 52%	50(1)	6.3	0.9
$(NH_4)_2SO_4$	20	1.9	12.5
NH_4NO_3	45	5.6	1.3

Operating Credits	Credit, \$
Flue Gas Desulfurization	0.50/T Coal Burned
Flue Gas Desulfurization	0.125/Bbl Oil Burned
Low End Temp. Corrosion Reduction	0.03/T Coal Burned
Low End Temp. Corrosion Reduction	0.0075/Bbl Oil Burned
Electrostatic Precipitator Power Credit	0.03/T Coal Burned
Limestone Calcining Thermal Debit	-0.03/T Coal Burned
Steam Production and Export	$0.50/10^6$ BTU

(1) 100% acid equivalent.

8.2.1 Catalytic Decomposition

Catalytic decomposition as a potential NO_x emission control technique was described in detail in Section 5.2 of this report. Catalytic decomposition is potentially the simplest of the NO_x flue gas emission control processes requiring only the addition of a catalytic reactor to the conventional boiler-flue-gas train. Figure 8-2 is a flow diagram of such a control process. Important assumptions that have been made in its design and costing are:

- The decomposition reactor is located upstream of the economizer where the temperature is about 900°F. No added cost is incurred in separating the economizer from the rest of the boiler.
- A high temperature electrostatic precipitator similar to one used in the Cat-OX process (8-2) is used in place of the conventional electrostatic precipitator to remove fly ash up stream of the catalyst.
- Added pressure drop is 6" H_2O through the reactor and 2" H_2O through the ducts for a total of 8" H_2O.
- Catalyst costs fall in the range of \$50 to \$300/ft^3 of catalyst and the process is operated at a space velocity of 6,000 to 7,000 SCFH/CF catalyst.
- The catalyst is resistant to sulfur and metals poisoning, but no decrease in SO_x emissions results from this process.
- The catalyst has an operating life of three years in a gas fired plant,and two years in either a coal or oil fired plant.
- 90% of the NO will be decomposed to N_2 and O_2.

Investment and operating costs for control of 1000 MW coal and oil burning power plants are detailed in Appendices 8-21 and 8-22 and for a 1000 MW gas burning plant in Appendices 8-23 and 8-24. Summaries of these costs are shown in Figures 8-3 and 8-4.

8.2.2 Selective Reduction

The use of H_2, NH_3, and H_2S as selective reductants for NO has been discussed in Section 5.3. An emission control process based on the catalyzed selective reduction of NO by hydrogen is shown in Figure 8-5. It is similar to the catalytic decomposition process except that the selective reduction reaction would be made to occur at lower temperatures to prevent hydrogen-oxygen reaction. Many of the same assumptions that were made in the design and costing of the catalytic decomposition process have been made for the selective hydrogen reduction process.

Figure 8-2

CATALYTIC DECOMPOSITION PROCESS

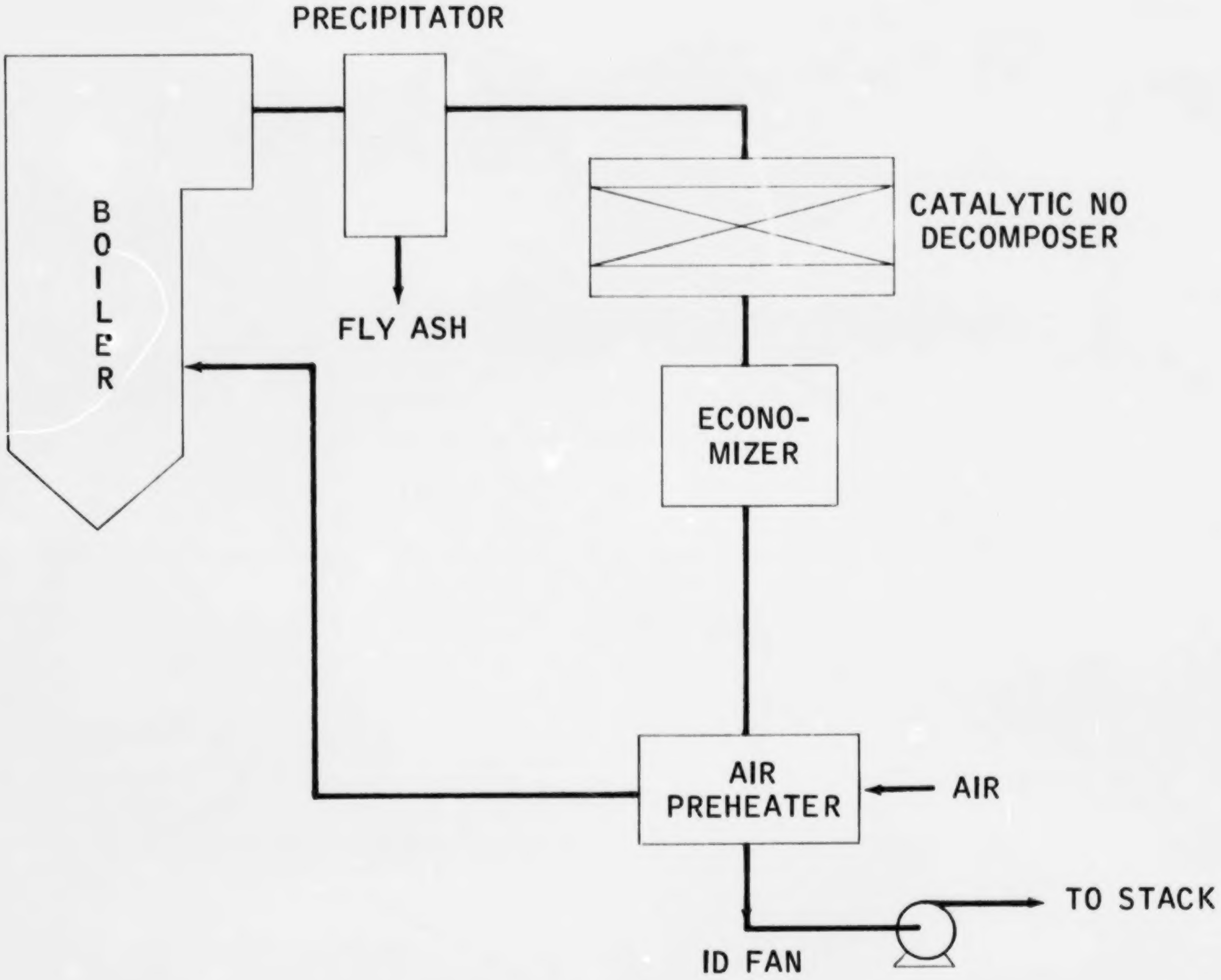

PRECIPITATOR
BOILER
FLY ASH
CATALYTIC NO DECOMPOSER
ECONO-MIZER
AIR PREHEATER
AIR
TO STACK
ID FAN

Figure 8-3

INVESTMENT COSTS FOR CATALYTIC DECOMPOSITION PROCESS

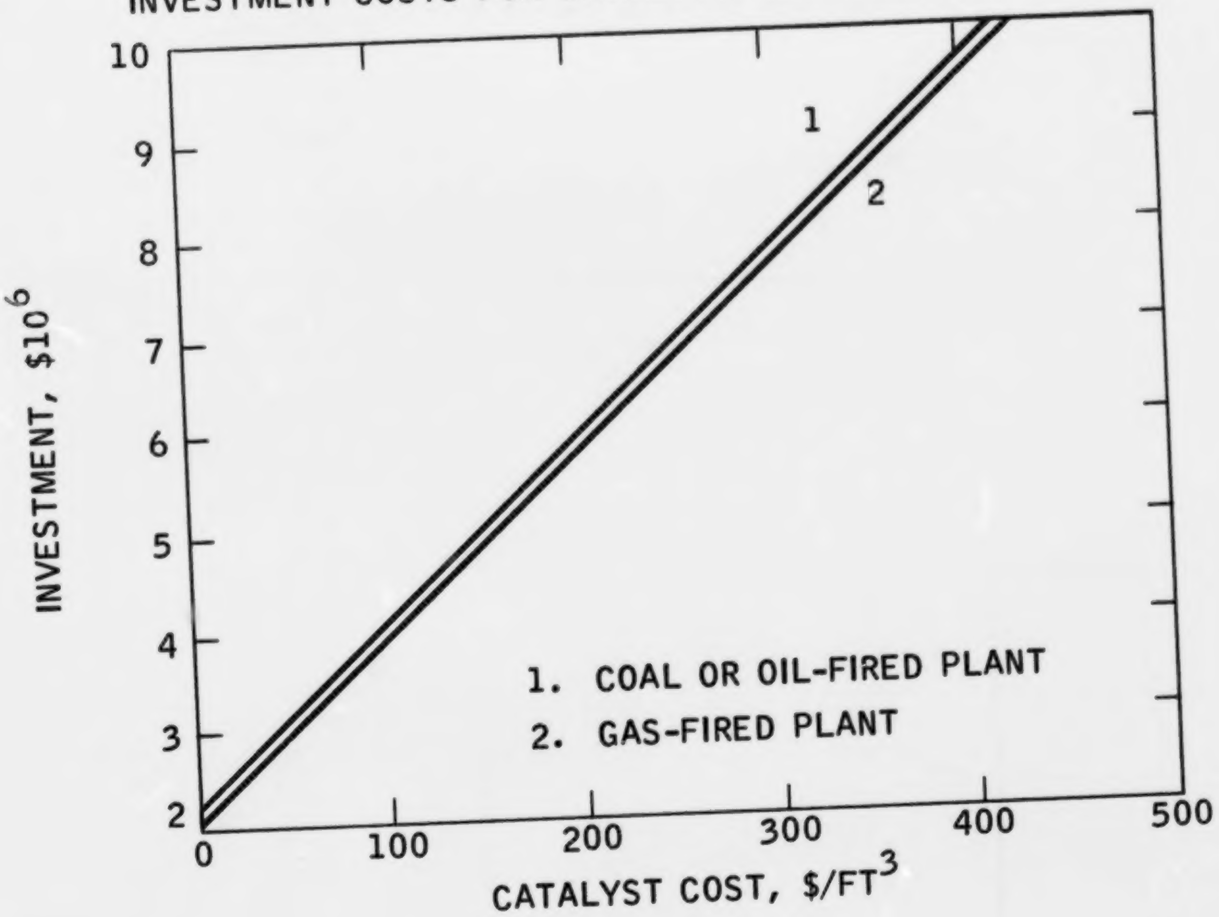
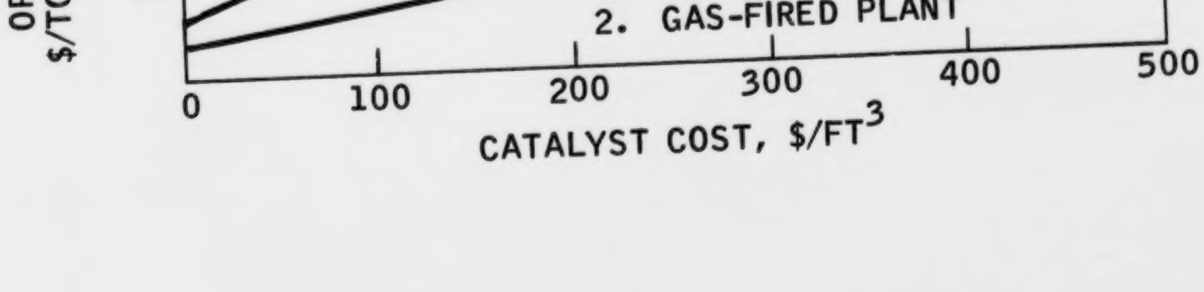


Figure 8-4

OPERATING COSTS FOR CATALYTIC DECOMPOSITION PROCESS



- The reduction reactor is located downstream of the economizer where the temperature is about 600°F.
- For a coal fired power plant, the electrostatic precipitator is repositioned between the economizer and the reactor at no increase in plant cost.
- Added pressure drop is 6" H_2O through the reactor and 2" H_2O through the ducts for a total of 8" H_2O.
- Catalyst costs will fall in the range of \$50 to \$300/ft^3 catalyst and the space velocity through the reactor is 6,000 to 7,000 SCFH/CF catalyst.
- The catalyst is resistant to sulfur and metals poisoning but no reduction in SO_x emission results from this process.
- The catalyst has an operating life of three years in a gas fired plant and two years in either a coal or oil fired plant.
- Addition of stoichiometric amounts of hydrogen (based on the NO reaction) results in 90% NO removal.

Appendices 8-21 and 8-25 contain the details of the investment and operating costs for control of 1000 MW coal and oil fueled power plants. In Appendices 8-23 and 8-26, costs for the gas fired plant are shown. Figures 8-6 and 8-7 provide summaries of the investment and operating costs as a function of assumed catalyst cost.

An NH_3 reduction system for gas fired power plants would closely resemble a hydrogen reduction system (Figure 8-5). Depending on the catalysts activity and selectivity (assuming a commercially acceptable catalyst became available), the reduction reactor would be located either upstream (~600°F) or downstream (~400°F) of the air preheater. Other assumptions made in the process design and cost estimate of the NH_3 reduction system are:

- Added pressure drop is 6" H_2O through the reactor and 2" H_2O through the ducts for a total of 8" H_2O.
- Catalyst costs fall in the range of \$50 to \$300/ft^3 catalyst and the space velocity through the reactor is 6,000 to 7,000 SCFH/CF catalyst. The catalyst has an operating life of three years.
- Ammonia is added in stoichiometric proportion of that needed for NO reaction and this results in 90% NO reduction.
- Ammonia is supplied directly from vendors tank cars.

Investment and operating costs developed on the basis of the above assumptions are given in Appendices 8-23 and 8-27. Highlights are shown in Figures 8-8 and 8-9.

Figure 8-5

CATALYTIC H_2 OR NH_3 REDUCTION PROCESS

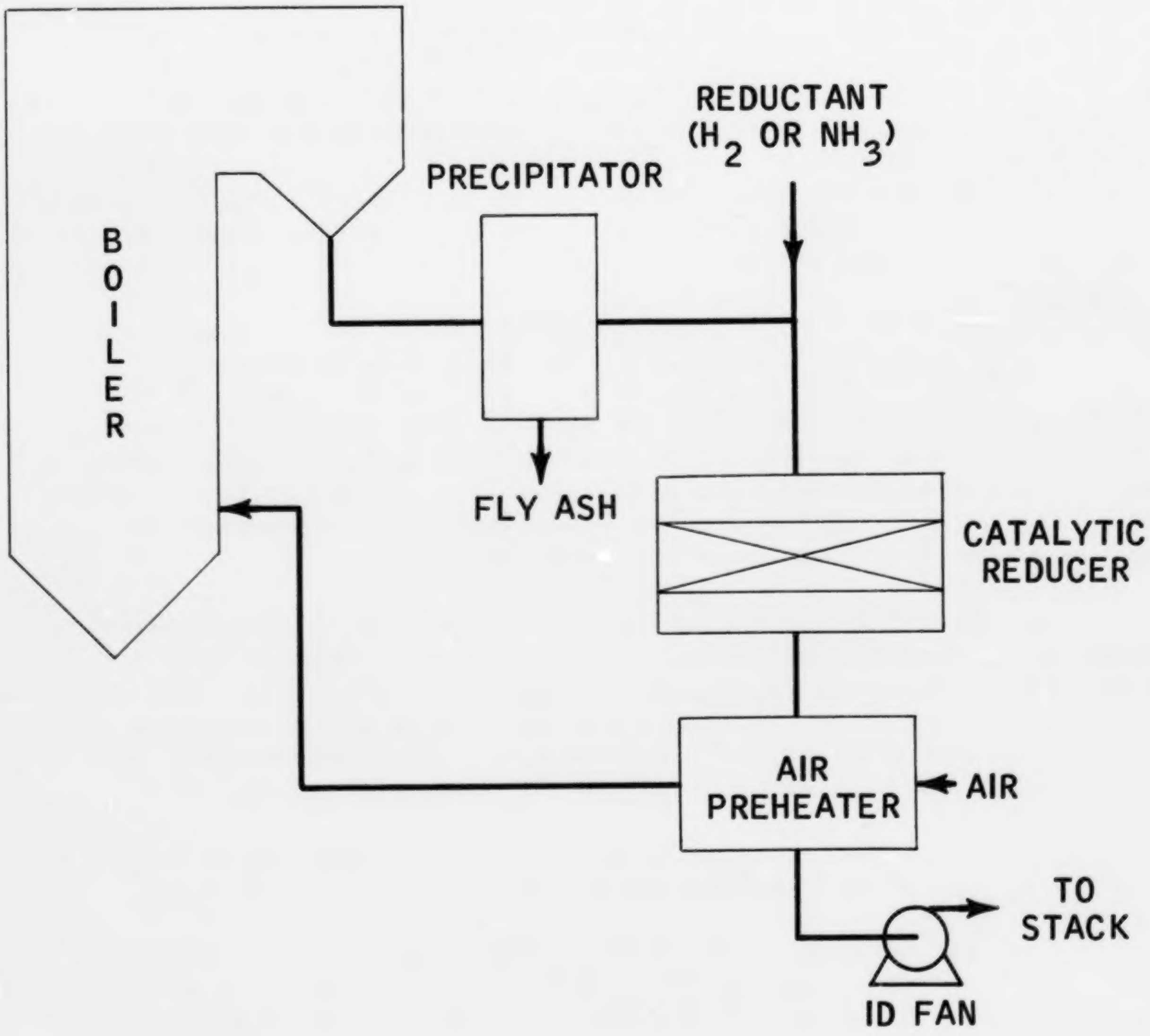

BOILER
PRECIPITATOR
REDUCTANT
(H_2 OR NH_3)
FLY ASH
CATALYTIC
REDUCER
AIR
PREHEATER
AIR
TO
STACK
ID FAN

Figure 8-6

INVESTMENT COSTS FOR CATALYTIC H_2 REDUCTION PROCESS

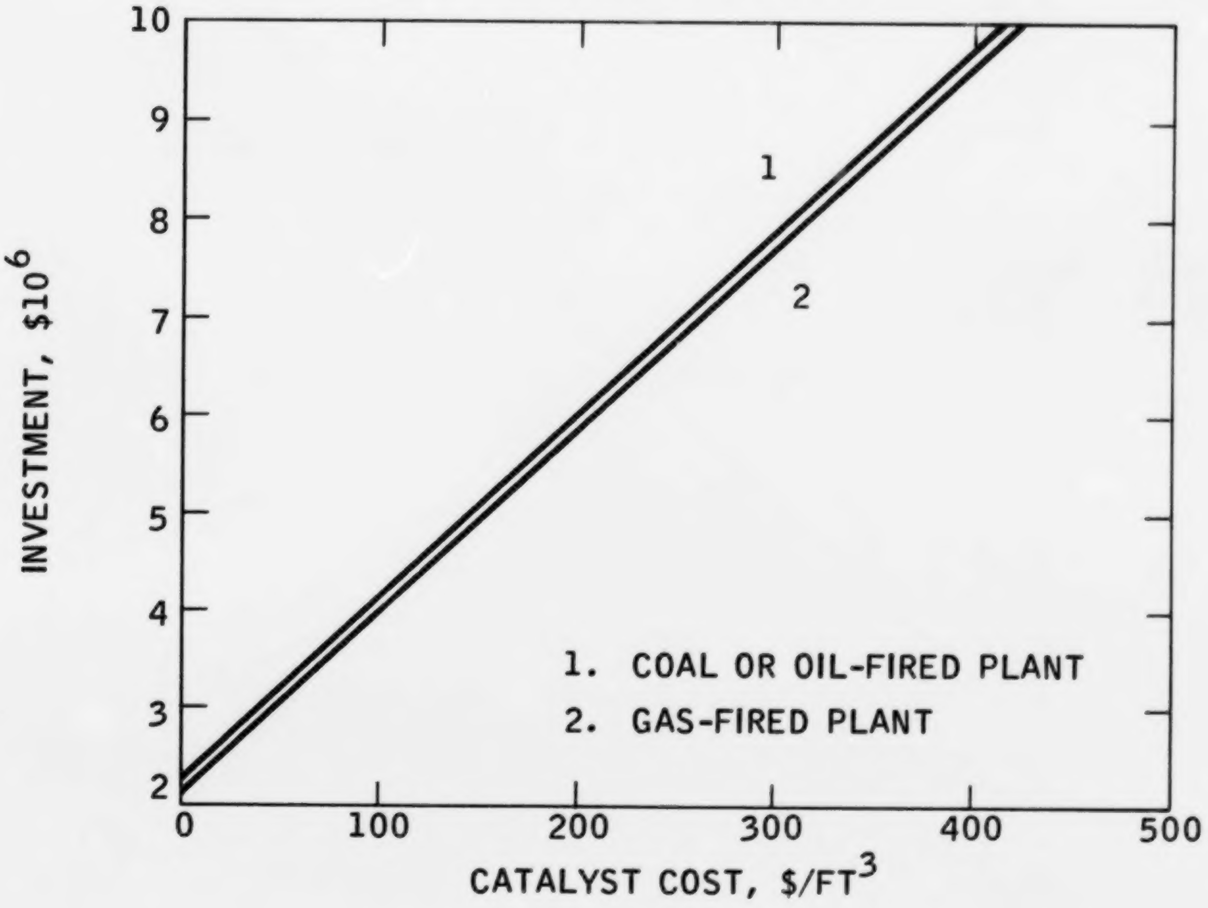


Figure 8-7

OPERATING COSTS FOR CATALYTIC H_2 REDUCTION PROCESS

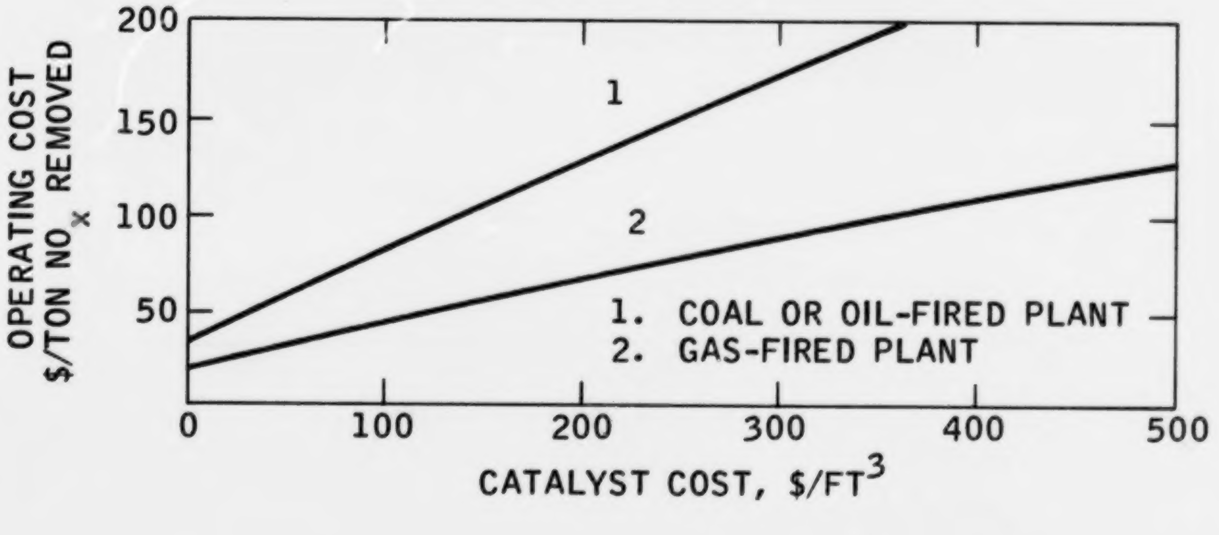


Figure 8-8

INVESTMENT COSTS FOR CATALYTIC NH_3 REDUCTION PROCESS IN A GAS-FIRED POWER PLANT

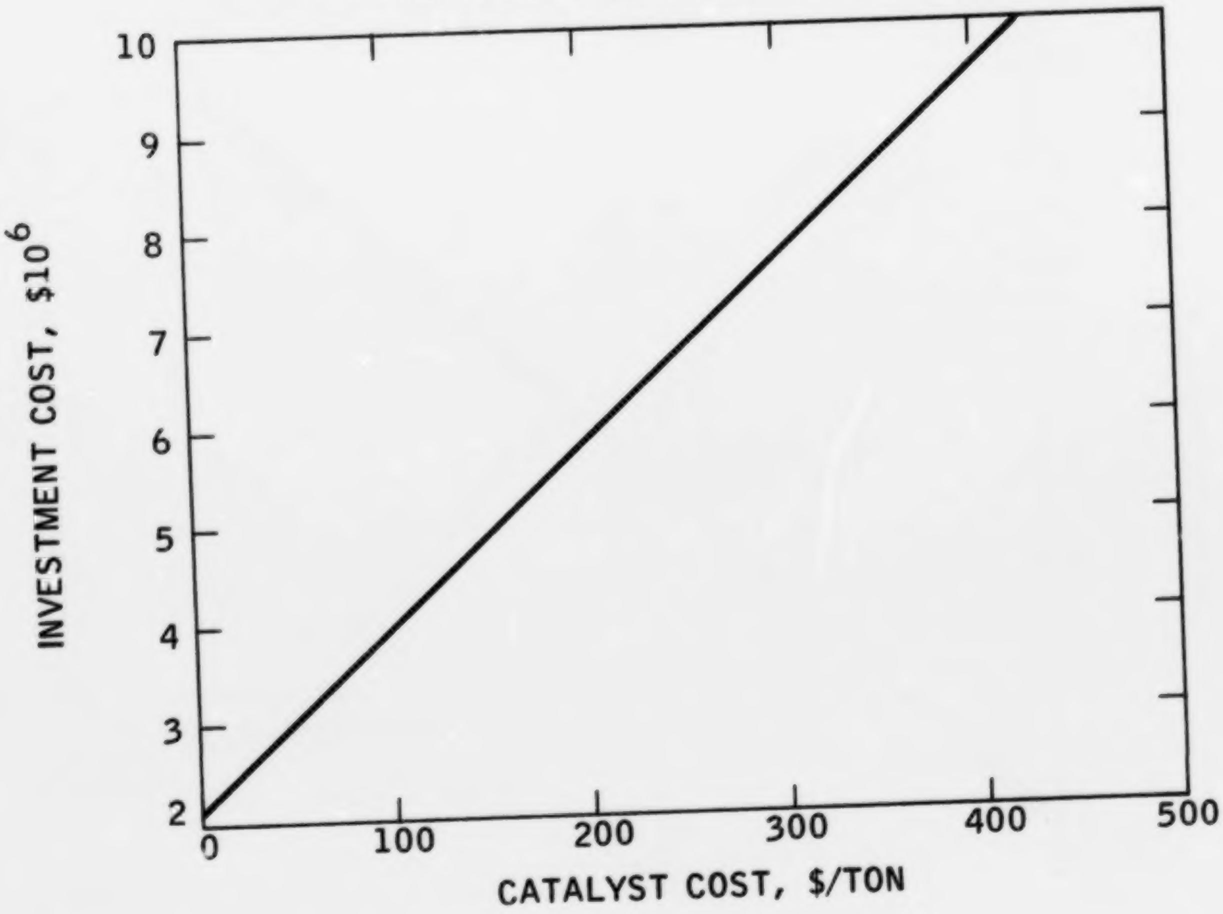
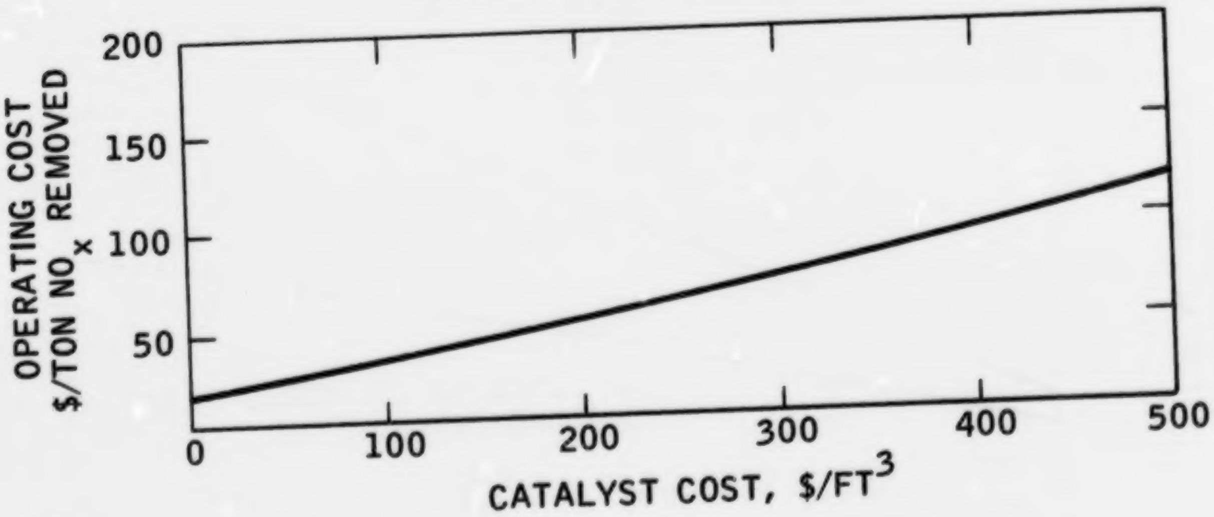


Figure 8-9

OPERATING COSTS FOR CATALYTIC NH_3 REDUCTION PROCESS IN A GAS-FIRED POWER PLANT



For coal or oil fired power plants, an NH_3 injection system could be designed to remove sulfur oxides in addition to nitrogen oxides. Figure 8-10 shows a flow diagram of a potential combined control system for a coal fired plant. Injected NH_3 first reacts with SO_3 and water to form $(NH_4)_2SO_4$ which is removed by precipitators from the gas stream. Additional NH_3 then selectively reduces the NO to nitrogen and water. The flue gas is then scrubbed with aqueous ammonia, the SO_2 reacting to form a mixture of NH_3HSO_3 and $(NH_3)_2SO_3$. In the mixing tank, the addition of more NH_3 converts some of the bisulfite to sulfite. Part of the solution leaving the mixing tank is returned to the scrubber and the rest is sent to an oxidizing tank where the solution is aerated to convert the ammonium sulfite-bisulfite to ammonium sulfate. The ammonium sulfate solution is then evaporated and the salt crystallized and dried for sale as fertilizer.

The assumptions that have been made in costing this NH_3 reduction-scrubbing process for the coal fired plant are:

- Added pressure drop is 6" H_2O through the reactor, 6" H_2O through the scrubbers and 2" H_2O through the ducts for a total of 14" H_2O.
- Catalyst costs and reactor space velocities are the same as for the gas fired plant.
- Ammonia addition is 100% of that stoichiometrically required for removal of nitrogen and sulfur oxides. Removal of sulfur oxides is 80% complete and removal of NO is 95% complete (90% by reduction at 5% by absorption).
- Ammonia is supplied directly from vendor's tank cars.

Investment and operating costs for control of the SO_x and NO_x emissions are given in Appendices 8-28 and 8-29 and are shown in summarized form in Figures 8-11 and 8-12. These costs are based on the standard operating and by-product credits listed in Table 8-16. The effect on control costs of changing the credits for the ammonium sulfate by-product is shown in Figure 8-12A.

Figure 8-10

NH_3 REDUCTION & SO_x SCRUBBING SYSTEM

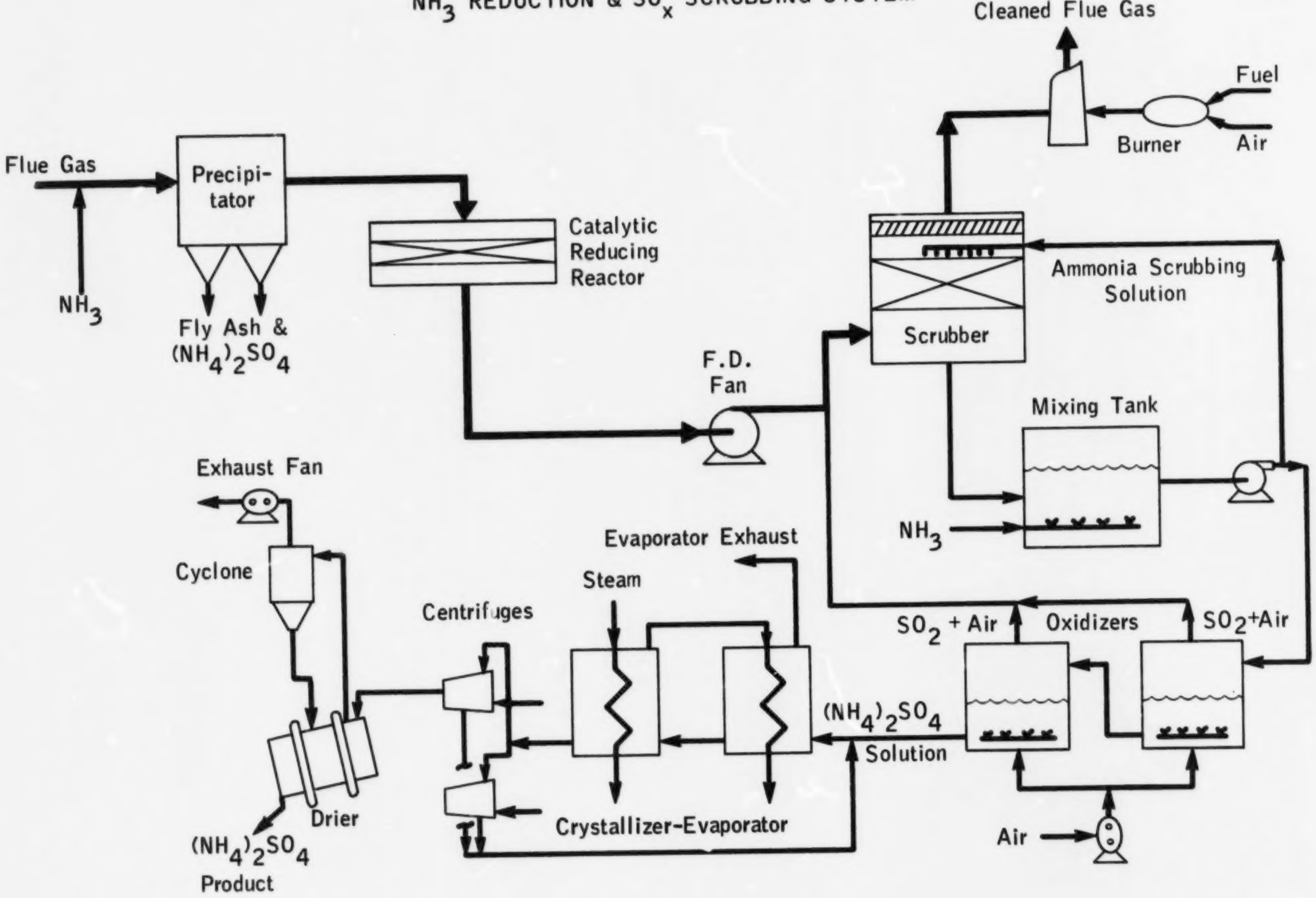

Cleaned Flue Gas
Fuel
Air
Burner
Flue Gas
Precipi-
tator
NH_3
Fly Ash &
$(NH_4)_2SO_4$
Catalytic
Reducing
Reactor
Ammonia Scrubbing
Solution
Scrubber
F.D.
Fan
Mixing Tank
NH_3
Exhaust Fan
Cyclone
Evaporator Exhaust
Steam
Centrifuges
SO_2 + Air
Oxidizers
SO_2+Air
$(NH_4)_2SO_4$
Solution
Drier
$(NH_4)_2SO_4$
Product
Crystallizer-Evaporator
Air

Figure 8-11

INVESTMENT COSTS FOR CATALYTIC NH_3 REDUCTION PROCESS WITH SO_2 EMISSION CONTROL IN COAL-FIRED PLANT

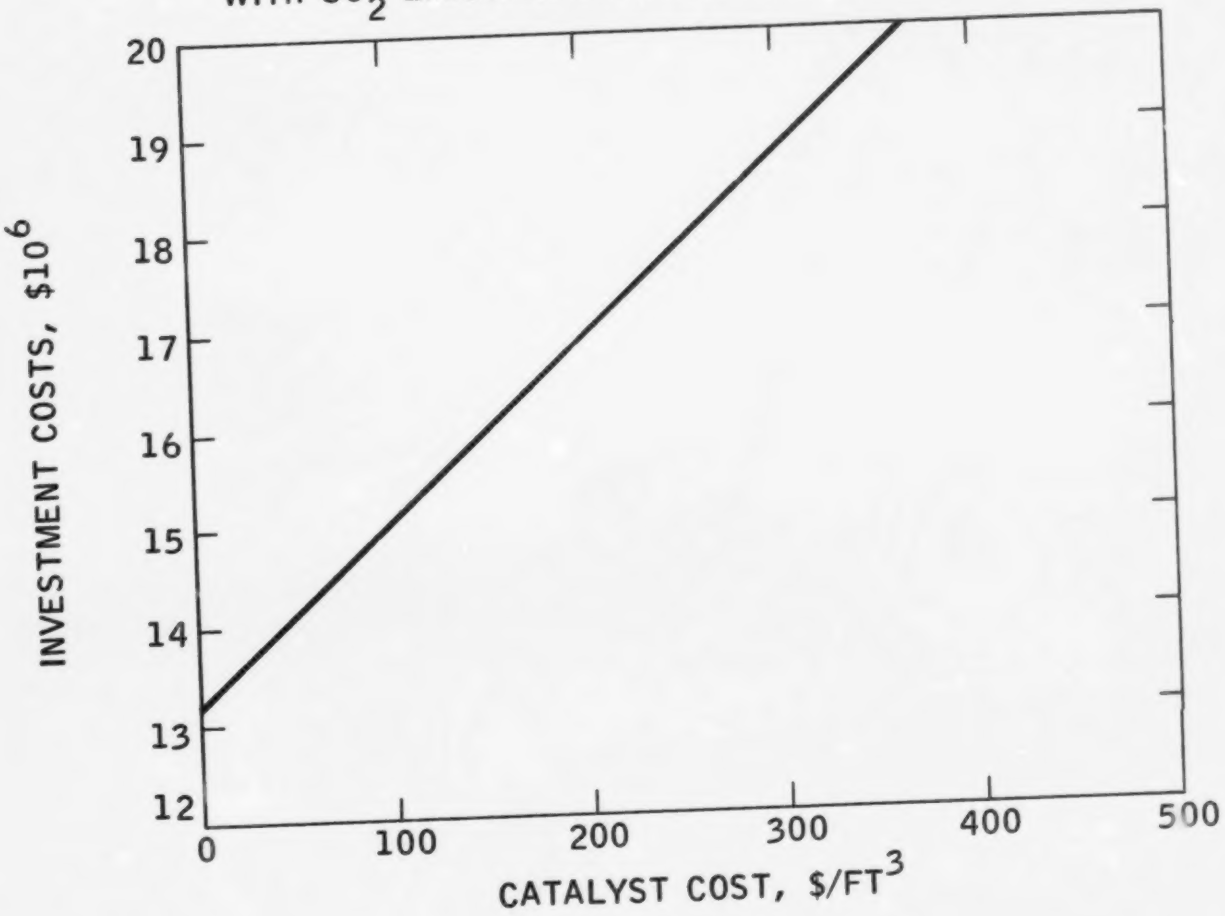


Figure 8-12

OPERATING COSTS FOR CATALYTIC NH_3 REDUCTION PROCESS WITH SO_2 EMISSION CONTROL IN COAL-FIRED PLANT

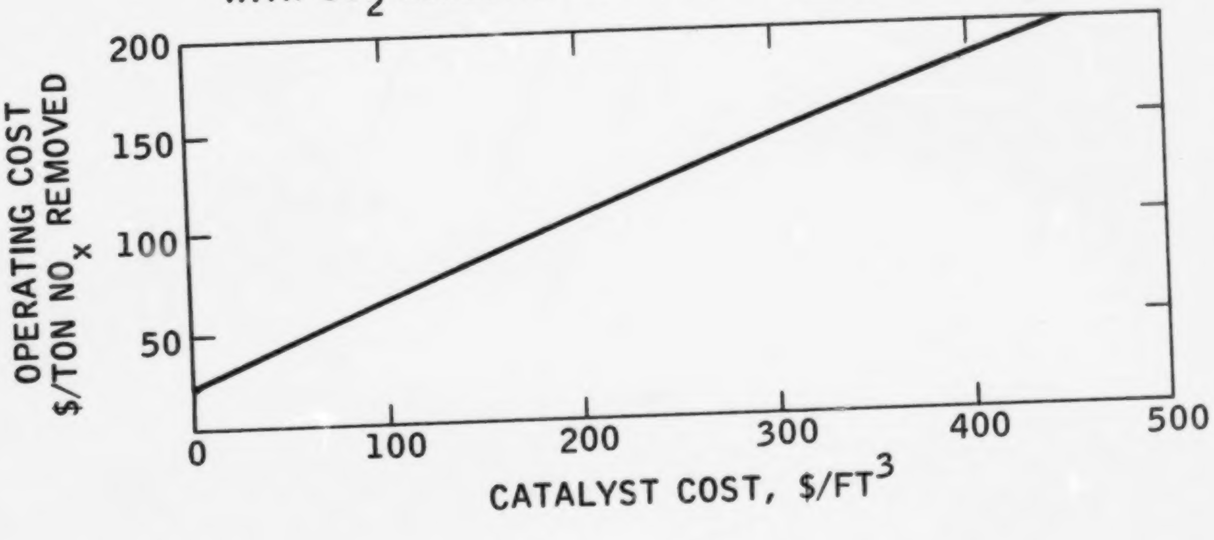
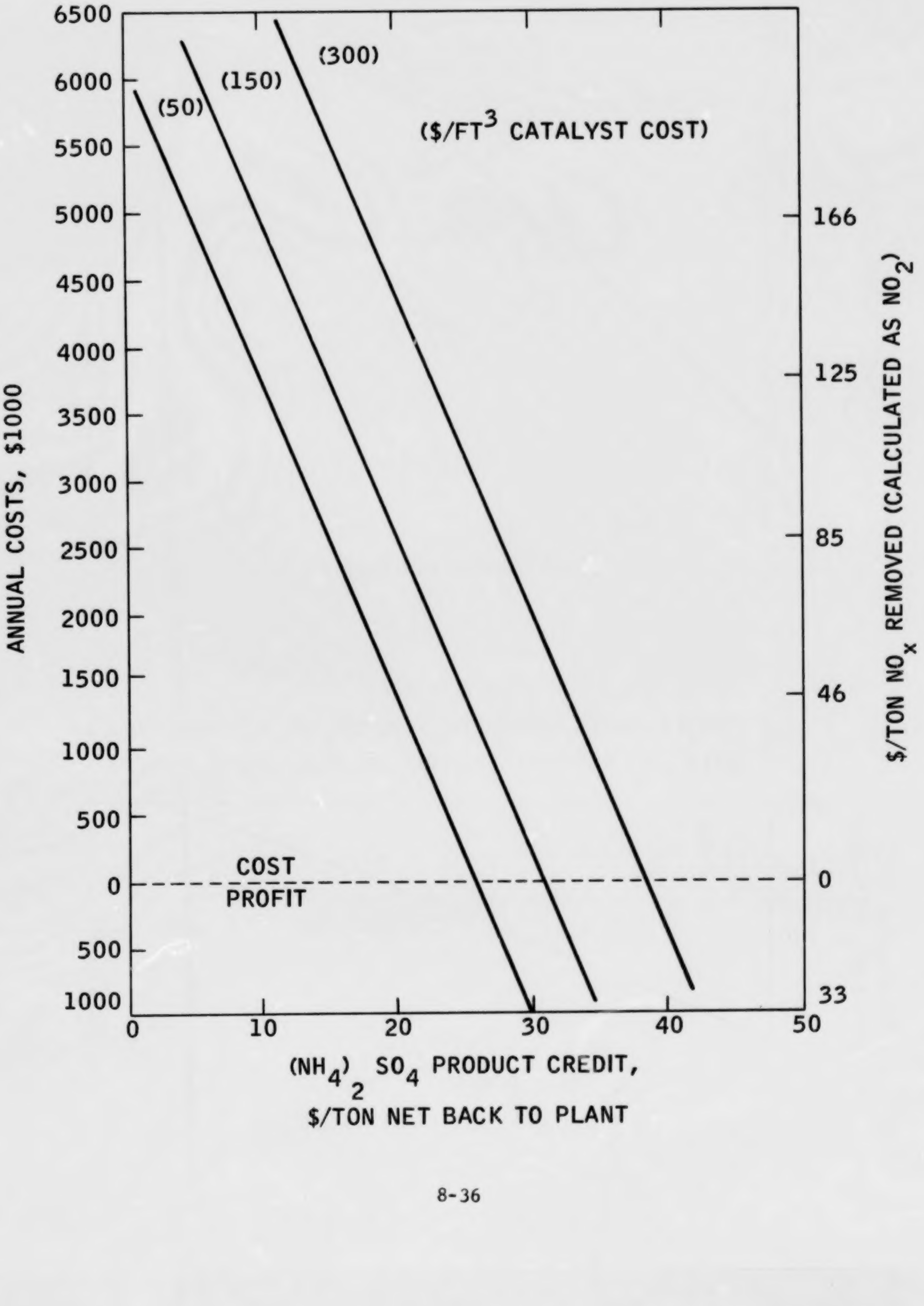


Figure 8-12A

SENSITIVITY OF CONTROL COSTS TO BY-PRODUCT CREDIT - CATALYTIC NH_3 PROCESS FOR NO_x AND SO_x CONTROL

(1000 MW COAL-FIRED POWER PLANT)



A H_2S reduction system for control of nitrogen as well as sulfur oxides would be essentially the same as that used just for the control of sulfur oxides emissions but it would be larger and might require the use of a different catalyst. Figure 8-13 shows a flow diagram of the Princeton Chemical Research H_2S reduction process, described in Section 5.3.2.3 of this report. The main features of the process are the catalytic reduction of SO_2 (to S) and NO (to N_2) by H_2S injected into flue gas cooled in a spray tower to about 250°F; recovery of the sulfur by cyclically stripping the catalyst at about 900°F with an inert gas; and generating the H_2S needed by reacting part of the sulfur with natural gas and water over an alumina catalyst. The process has been designed with four catalyst beds. At any time, two of the beds are in the reduction cycle and are in different stages of deactivation, the third is being stripped and the fourth has been stripped and is being cooled in preparation for a reduction cycle.

In order to engineer and cost this process, the following major assumptions have been made:

- A molecular sieve reducing catalyst is used and its operating life is five years. Space velocity through the reducing reactor is about 16.7 SCFH/lb catalyst.

- Pressure drop through the system is 15" H_2O of which 13" H_2O is in the reactor and 2" H_2O in the ducts.

- Only 90% of the H_2S required for complete removal is recycled in order to avoid H_2S emissions. 90% of the sulfur and nitrogen oxide are removed.

Detailed investment and operating costs for this process are shown in Appendix 8-30 and 8-31, respectively, for a 1000 MW coal burning plant. Total plant investment for installing this process in such a plant is computed to be $11,680,000 and the annual operating cost after deducting standard product and operating credits (Table 8-16) is $2,091,000 or about $77/ton NO_x removed (calculated as NO_2). The effect on control costs of changing the by-product sulfur credit is shown in Figure 8-13A.

Figure 8-13

CATALYTIC H_2S REDUCTION PROCESS FOR NO_x AND SO_x EMISSION CONTROL

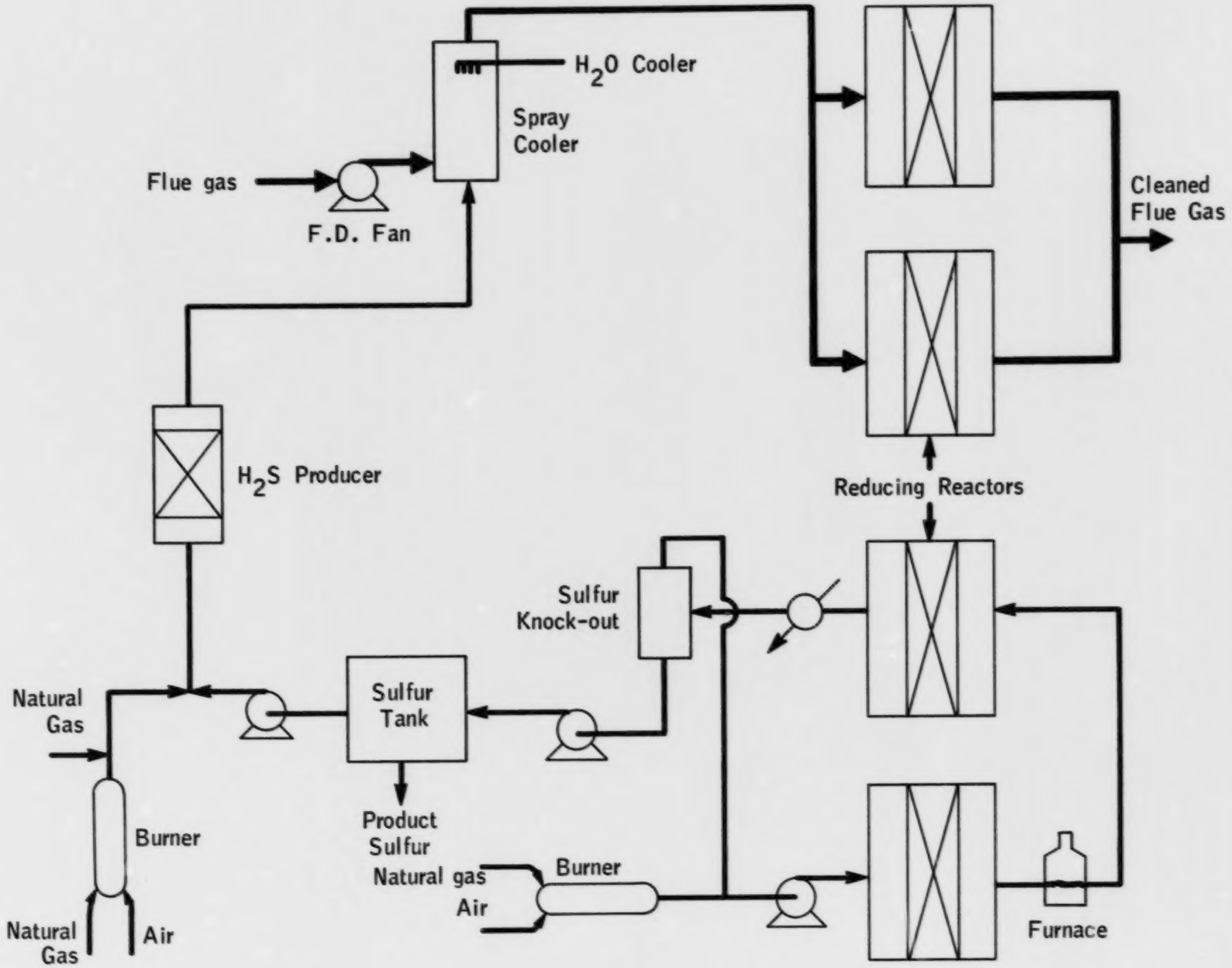
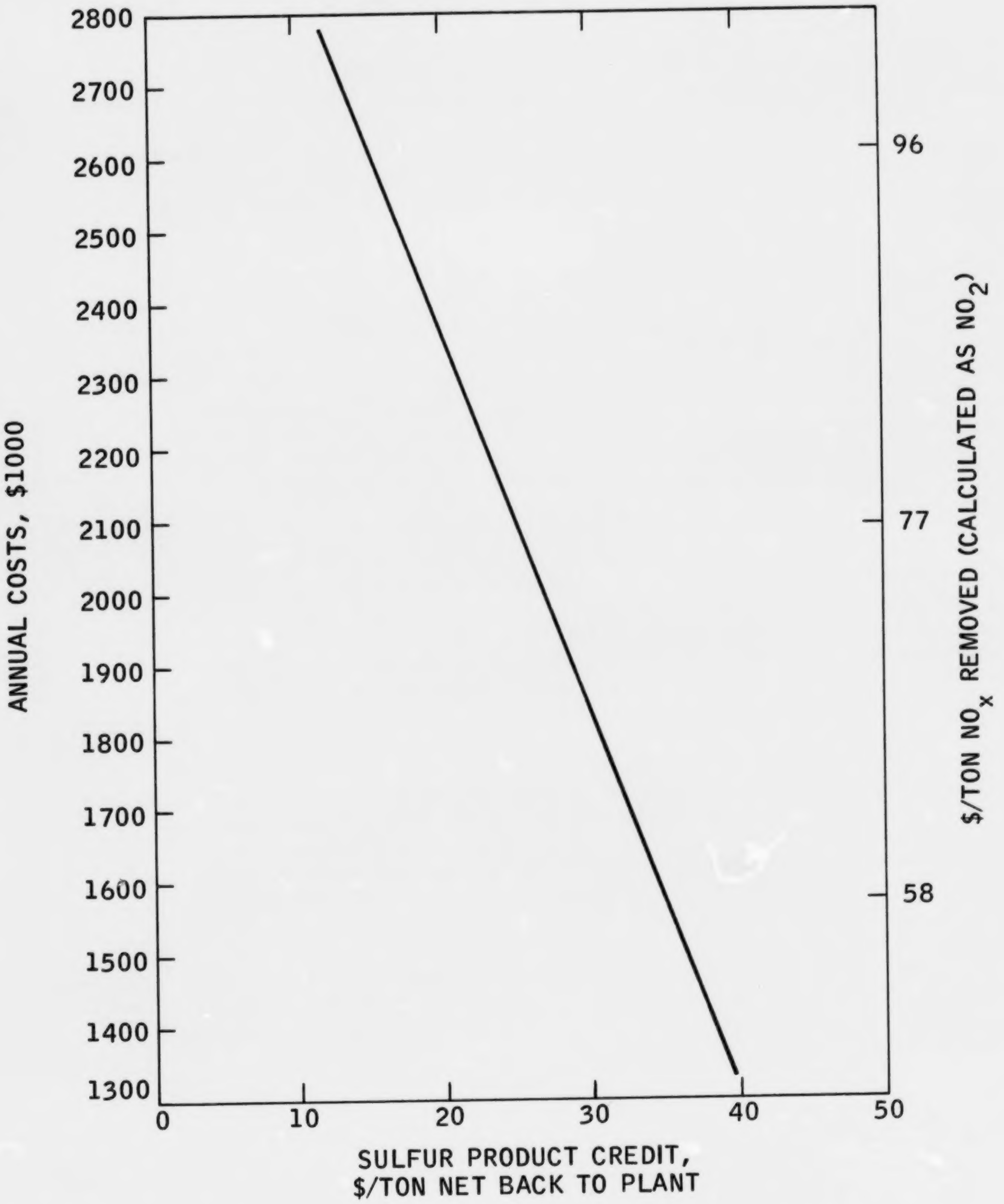

H_2O Cooler
Spray Cooler
Flue gas
F.D. Fan
Cleaned Flue Gas
H_2S Producer
Reducing Reactors
Sulfur Knock-out
Natural Gas
Sulfur Tank
Product Sulfur
Burner
Natural gas
Air
Burner
Natural Gas
Air
Furnace

Figure 8-13A

SENSITIVITY OF CONTROL COSTS TO BY-PRODUCT CREDIT - CATALYTIC H_2S REDUCTION PROCESS FOR SO_x AND NO_x CONTROL (1000 MW COAL-FIRED POWER PLANT)



8.2.3 Alkaline Scrubbing Systems

The use of $Ca(OH)_2$ and $Mg(OH)_2$ scrubbing systems for control of both sulfur and nitrogen oxide emissions is described in section 5.6.2 of this report. These systems involve the recycle of NO_2 to the flue gas to achieve an equimolar NO-NO_2 mixture which then reacts with the aqueous alkaline solutions to form predominantly nitrite salts. The NO_2 that is recycled is obtained by decomposing these salts and oxidizing the NO formed to NO_2.

Figures 8-14 and 8-15 show the flow diagrams of two potential $Ca(OH)_2$ scrubbing systems for controlling emissions from coal or oil fired power plants. Both systems involve the use of two scrubbers in order to separate the removal of fly ash and sulfur oxides from the removal of the nitrogen oxides. The recycle NO_2 is added to the cooled, relatively SO_2 free gas between the two scrubbers to minimize reaction between SO_2 and NO_2.

The two processes differ in their method of decomposing the nitrite salts that are formed. In the process shown in Figure 8-14, a portion of the scrubber effluent is acidified with H_2SO_4 to liberate NO. A mixture of $CaSO_4$ and $Ca(NO_3)_2$ are produced. In the process shown in Figure 8-15, the nitrite solution is evaporated and the salts decomposed at about 1300°F in a fluidized bed through which hot combustion gases produced by burning natural gas are passed. The hot NO-rich gas from the fluidized bed is able to produce enough steam for use in the evaporator and to generate some additional power in the plant.

The NO-rich gas produced by either the acid or thermal decomposition is passed through an oxidizer-absorber tower where HNO_3 and NO_2 are produced. The tower is water cooled and contains thin layers of char catalyst to promote the NO oxidation. The nitric acid produced is sold to offset processing costs and the NO_2 is injected into the flue gas. Major assumptions that have been made in costing this process are:

- The power plant has available land for discharging the fly ash, $CaSO_4$ and $Ca(NO_3)_2$, and such discharging is not restricted by pollution of nearby lakes or streams.
- The scrubbers have been assumed to be about the same size as those used by TVA in its study of limewater scrubbing of flue gas (8-3).
- 90% removal efficiency of sulfur and nitrogen oxides is obtained. Pressure drop through each scrubber is 6" H_2O and pressure drop through the added ductwork is 2" H_2O.

Figure 8-14

TWO-SCRUBBER LIMEWATER CONTROL SYSTEM WITH ACID DECOMPOSITION

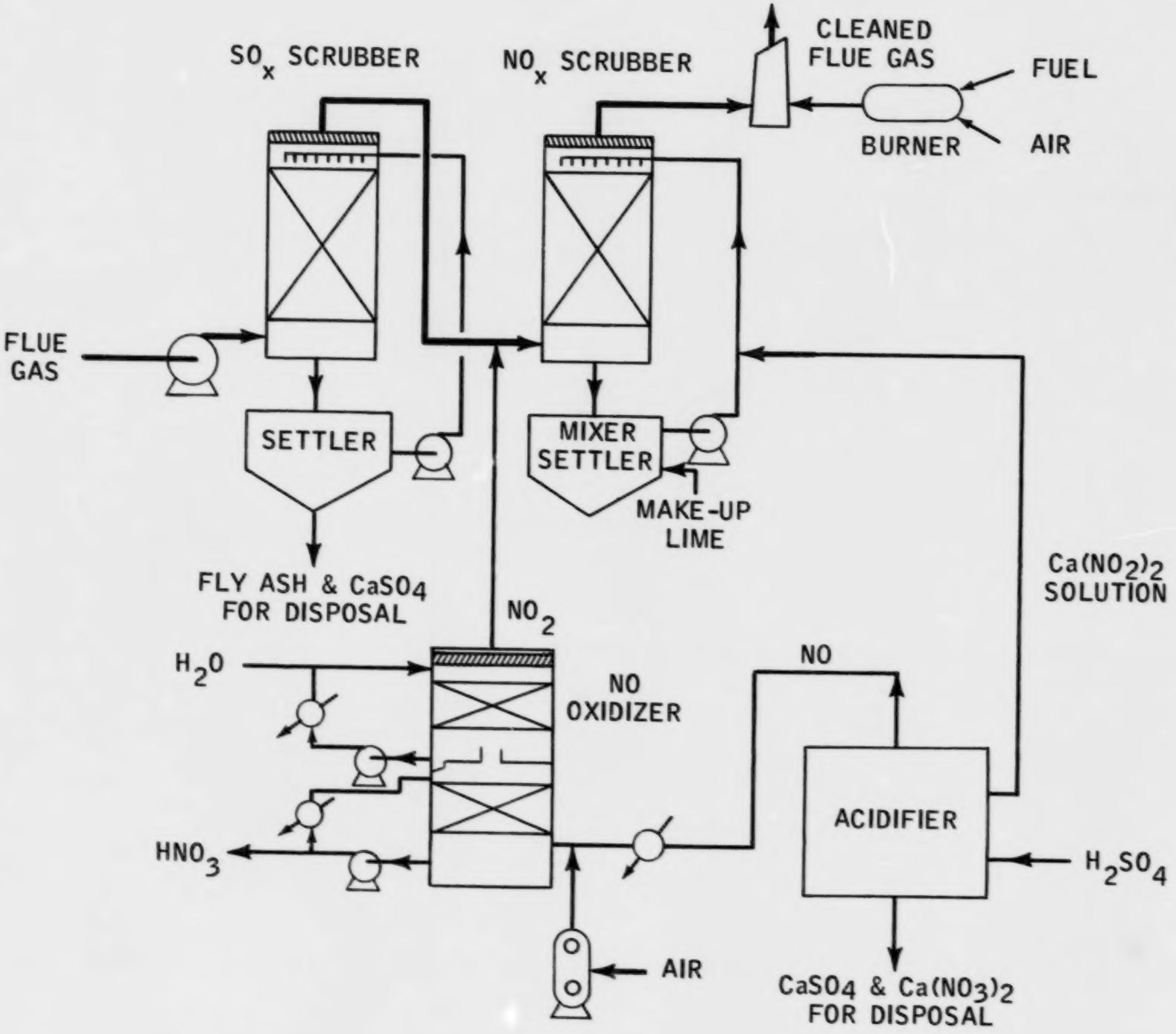
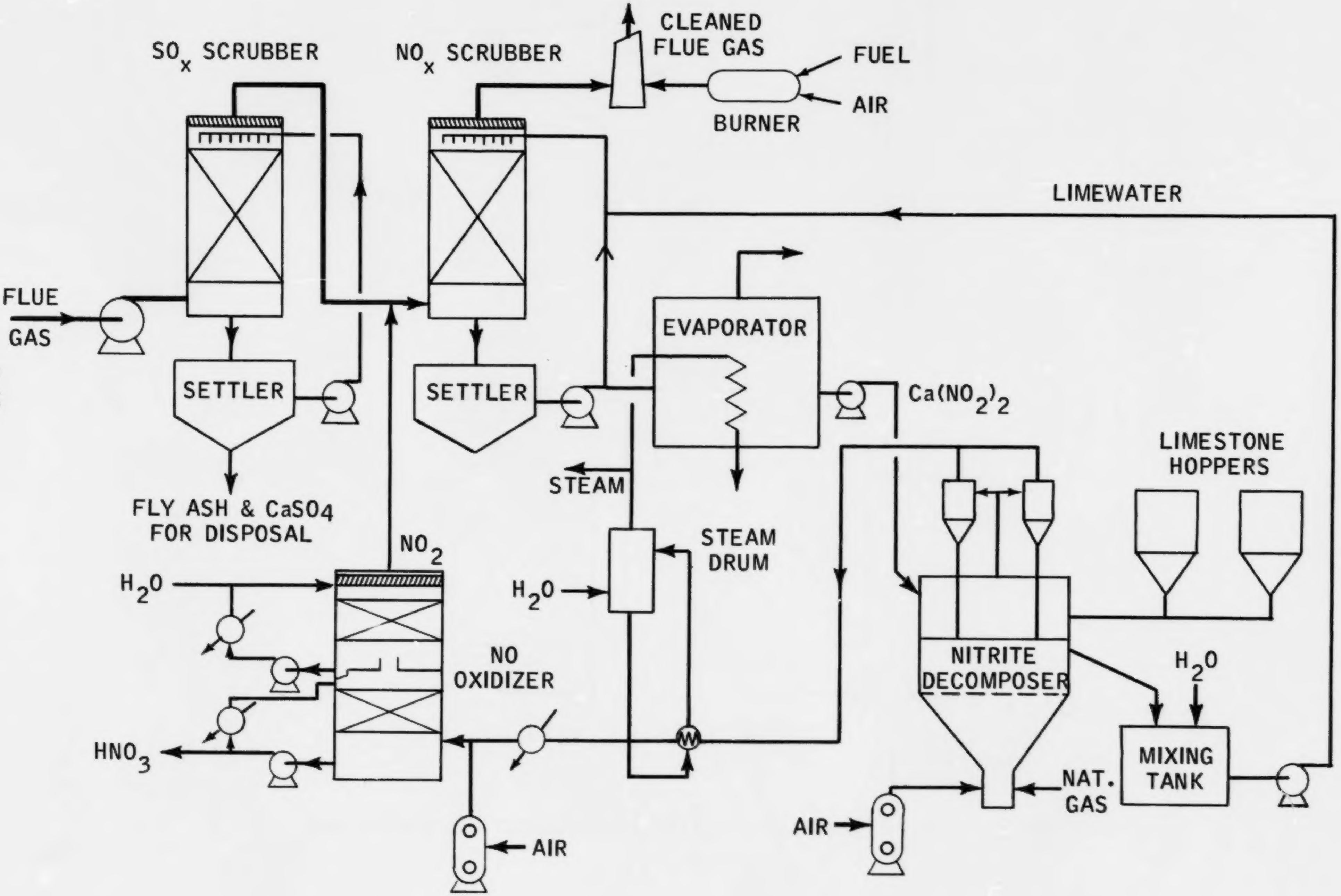

SO_x SCRUBBER
NO_x SCRUBBER
CLEANED FLUE GAS
FUEL
BURNER
AIR
FLUE GAS
SETTLER
MIXER SETTLER
MAKE-UP LIME
FLY ASH & $CaSO_4$ FOR DISPOSAL
NO_2
$Ca(NO_2)_2$ SOLUTION
H_2O
NO OXIDIZER
NO
ACIDIFIER
HNO_3
H_2SO_4
AIR
$CaSO_4$ & $Ca(NO_3)_2$ FOR DISPOSAL

Figure 8-15

TWO-SCRUBBER LIMEWATER CONTROL SYSTEM WITH THERMAL DECOMPOSITION


SO$_x$ SCRUBBER
NO$_x$ SCRUBBER
CLEANED FLUE GAS
FUEL
AIR
BURNER
LIMEWATER
FLUE GAS
EVAPORATOR
SETTLER
SETTLER
Ca(NO$_2$)$_2$
LIMESTONE HOPPERS
STEAM
FLY ASH & CaSO4 FOR DISPOSAL
NO$_2$
STEAM DRUM
H$_2$O
H$_2$O
NO OXIDIZER
NITRITE DECOMPOSER
H$_2$O
HNO$_3$
MIXING TANK
NAT. GAS
AIR
AIR

- Sufficient make-up lime or limestone is added to the second scrubber to maintain an alkaline solution throughout this scrubber.

- Make-up limestone for SO_x removal is injected into the furnace where it reacts with all the SO_3 (and some of the SO_2) thereby reducing low temperature corrosion.

- Sulfuric acid for the acid decomposition is supplied directly from a vendor's tank car, i.e., no storage tanks are needed, and no demurrage charge for delay in unloading is assumed.

Figure 8-16 shows a thermal decomposition process using only a single scrubber for removal of fly ash, sulfur oxides and nitrogen oxides. This system was evaluated as an alternate to that in Figure 8-15 since a separate SO_x scrubber may not be needed if the SO_2-NO_2 reaction could be made sufficiently slow by cooling the flue gas. To cool the gas, a water spray tower located upstream of the NO_2 injection point has been assumed to be sufficient. Fly ash and some of the sulfur oxide are removed in this tower. After addition of the NO_2 recycle, the nitrogen oxides and the remaining sulfur oxides are removed in the absorber. For a gas fired power plant, NO_x control requires only the single scrubber system and the spray tower is not needed.

Details of investment and operating costs for the different limewater scrubbing systems are to be found in Appendices 8-32 through 8-41. A summary of these costs, based on standard operating and by-product credits (Table 8-16), is given in Table 8-17. Figures 8-16A, B, C, D and E show the sensitivity of control costs to changing nitric acid by-product credits.

Table 8-17

Summary of Emission Control Costs
For 1000 MW Power Plant Using Limewater Scrubbing

Control Process	Net Investment	Operating Costs Annual	Operating Costs $/Ton NO_x Removed*
Coal Plant, 2 Scrubbers, Acid Decomp.	7,783,000	2,800,000	117
Coal Plant, 2 Scrubbers, Thermal Decomp.	10,383,000	1,671,000	70
Coal Plant, 1 Scrubber, Thermal Decomp.	8,472,000	1,071,000	45
Oil Plant, 1 Scrubber, Thermal Decomp.	9,011,000	1,194,000	50
Gas Plant, 1 Scrubber, Thermal Decomp.	9,742,000	929,000	22

* Calculated as NO_2.

Figure 8-16

SINGLE SCRUBBER LIMEWATER CONTROL SYSTEM WITH THERMAL DECOMPOSITION

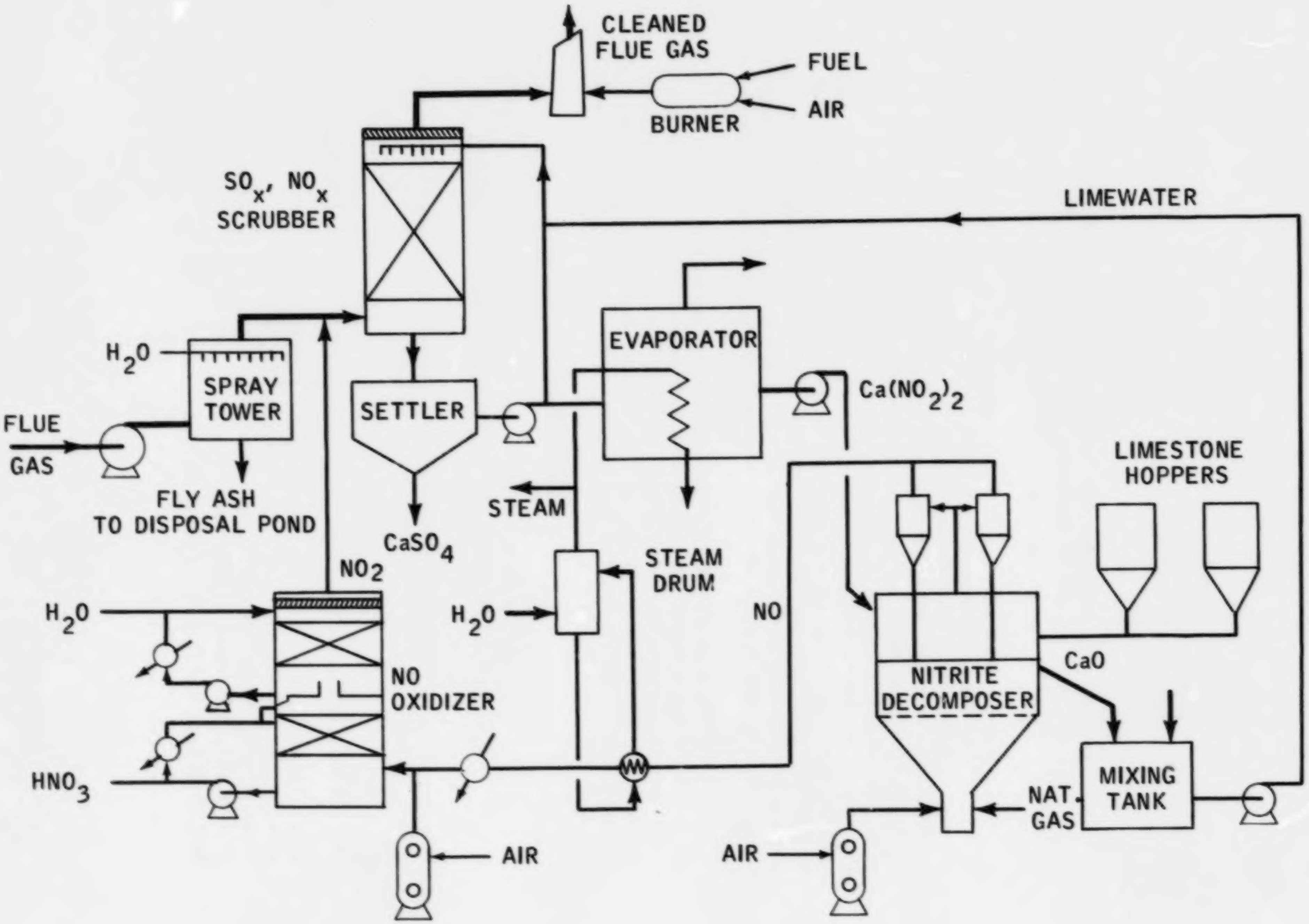

CLEANED FLUE GAS
FUEL
AIR
BURNER
SO_x, NO_x SCRUBBER
LIMEWATER
EVAPORATOR
H_2O
SPRAY TOWER
FLUE GAS
FLY ASH TO DISPOSAL POND
SETTLER
$Ca(NO_2)_2$
LIMESTONE HOPPERS
STEAM
$CaSO_4$
NO_2
STEAM DRUM
NO
H_2O
H_2O
NO OXIDIZER
NITRITE DECOMPOSER
CaO
HNO_3
MIXING TANK
NAT. GAS
AIR
AIR

Figure 8-16A

SENSITIVITY OF CONTROL COSTS
TO BY-PRODUCT CREDIT -
TWO-SCRUBBER LIMEWATER PROCESS
WITH ACID DECOMPOSITION
(1000 MW COAL-FIRED POWER PLANT)

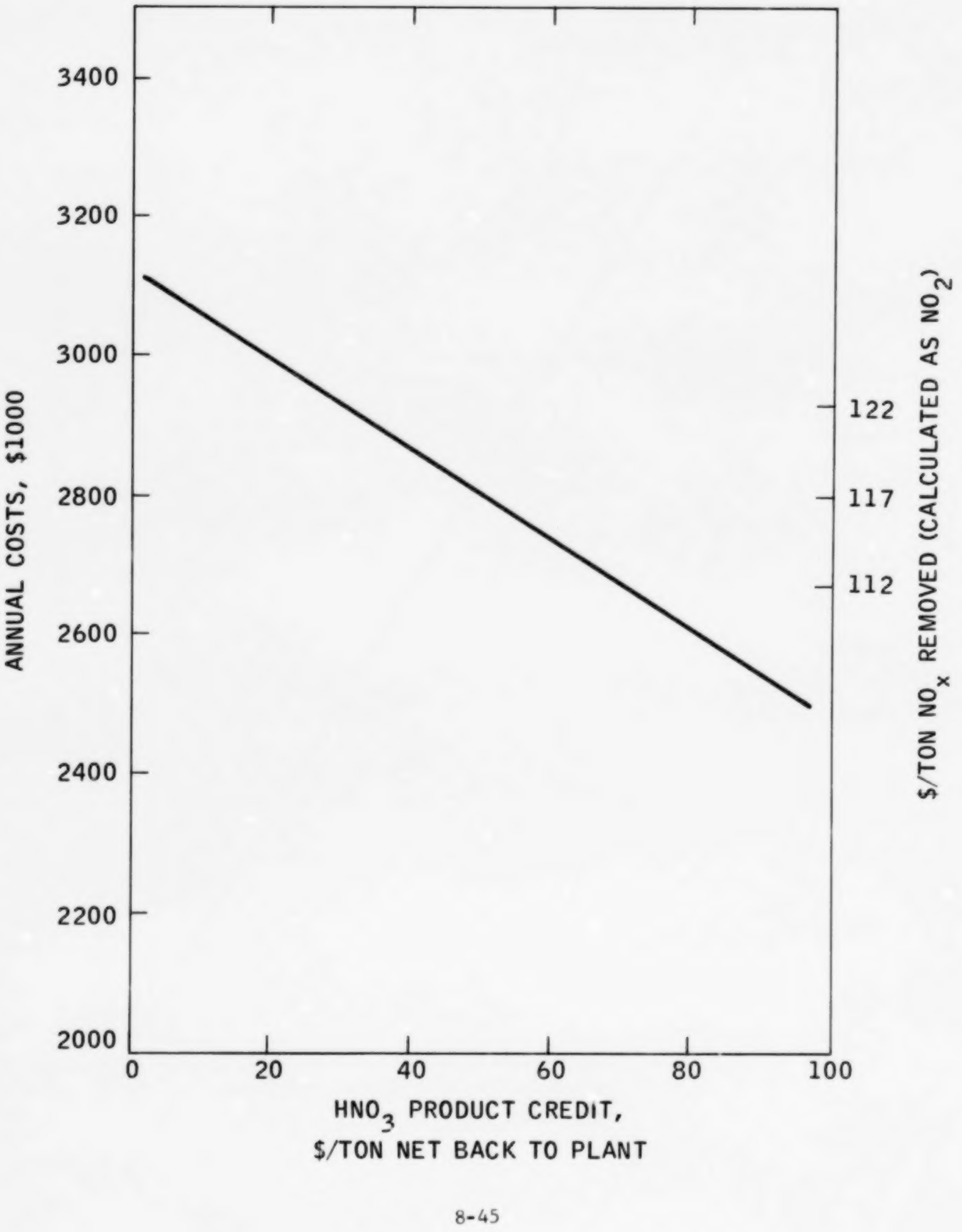


Figure 8-16B

SENSITIVITY OF CONTROL COSTS
TO BY-PRODUCT CREDIT -
TWO-SCRUBBER LIMEWATER PROCESS
WITH THERMAL DECOMPOSITION
(1000 MW COAL-FIRED POWER PLANT)

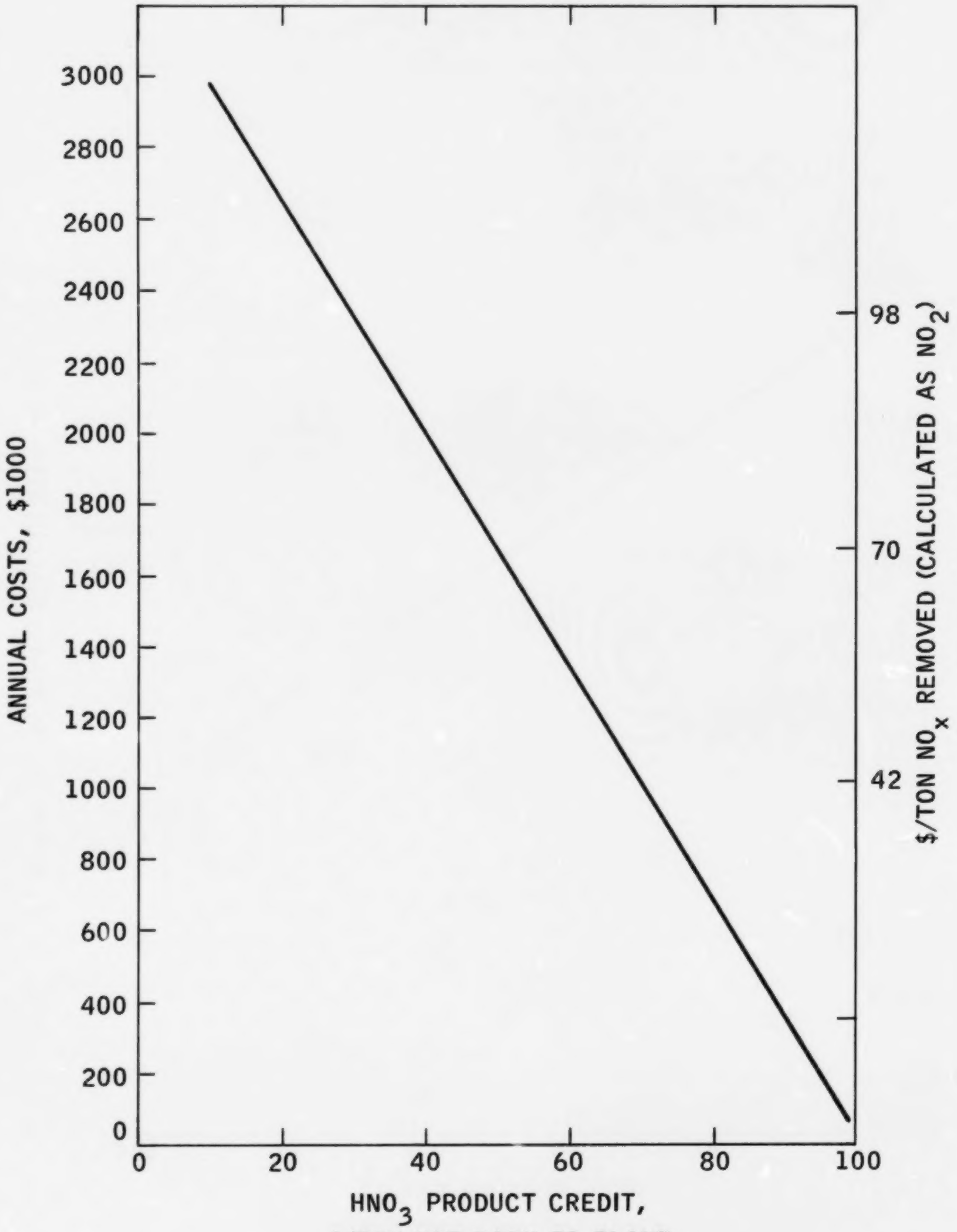


Figure 8-16C

SENSITIVITY OF CONTROL COSTS
TO BY-PRODUCT CREDIT -
SINGLE SCRUBBER LIMEWATER PROCESS
WITH THERMAL DECOMPOSITION
(1000 MW COAL-FIRED POWER PLANT)

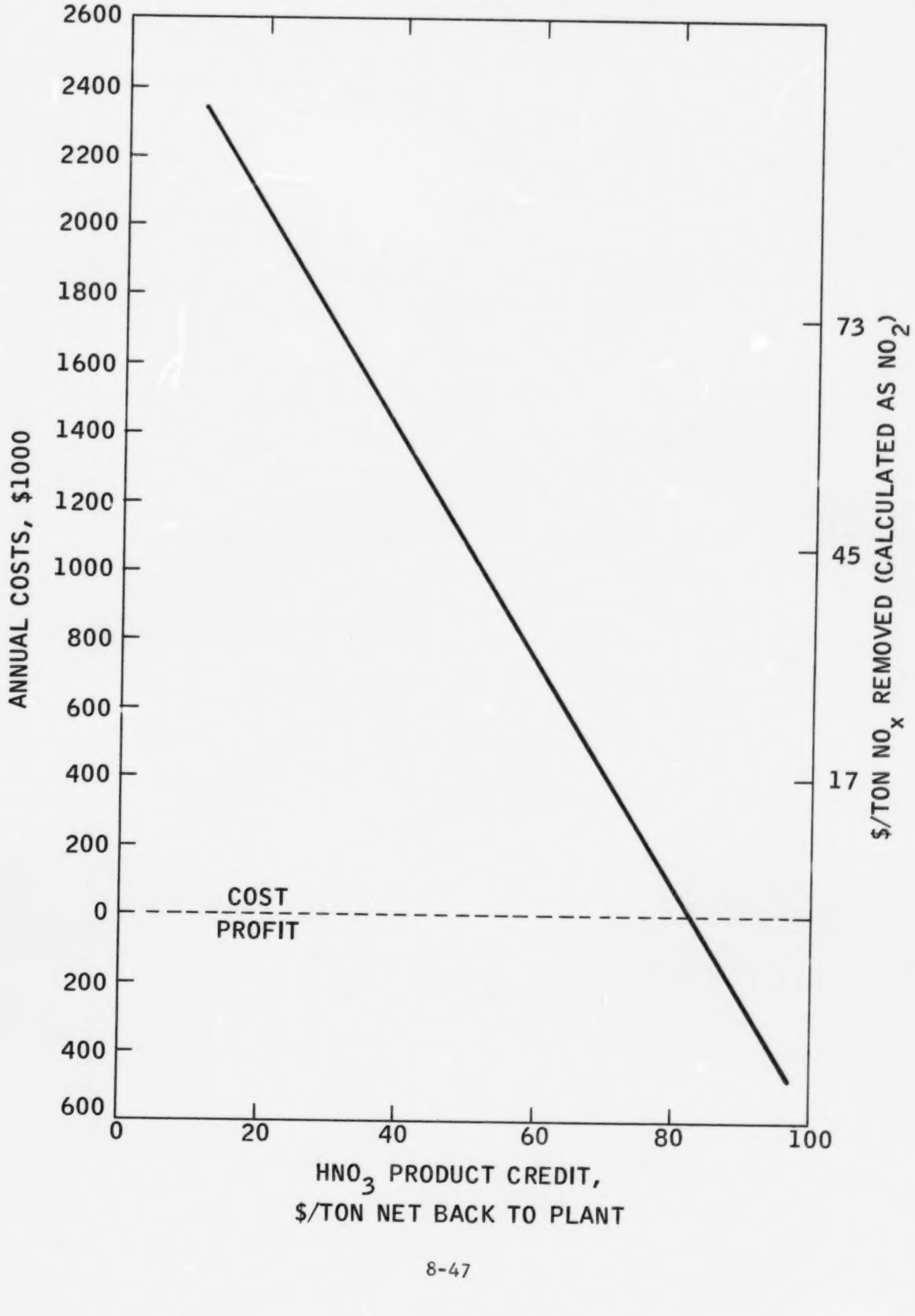


Figure 8-16D

SENSITIVITY OF CONTROL COSTS
TO BY-PRODUCT CREDIT -
SINGLE SCRUBBER LIMEWATER PROCESS
WITH THERMAL DECOMPOSITION
(1000 MW OIL-FIRED POWER PLANT)

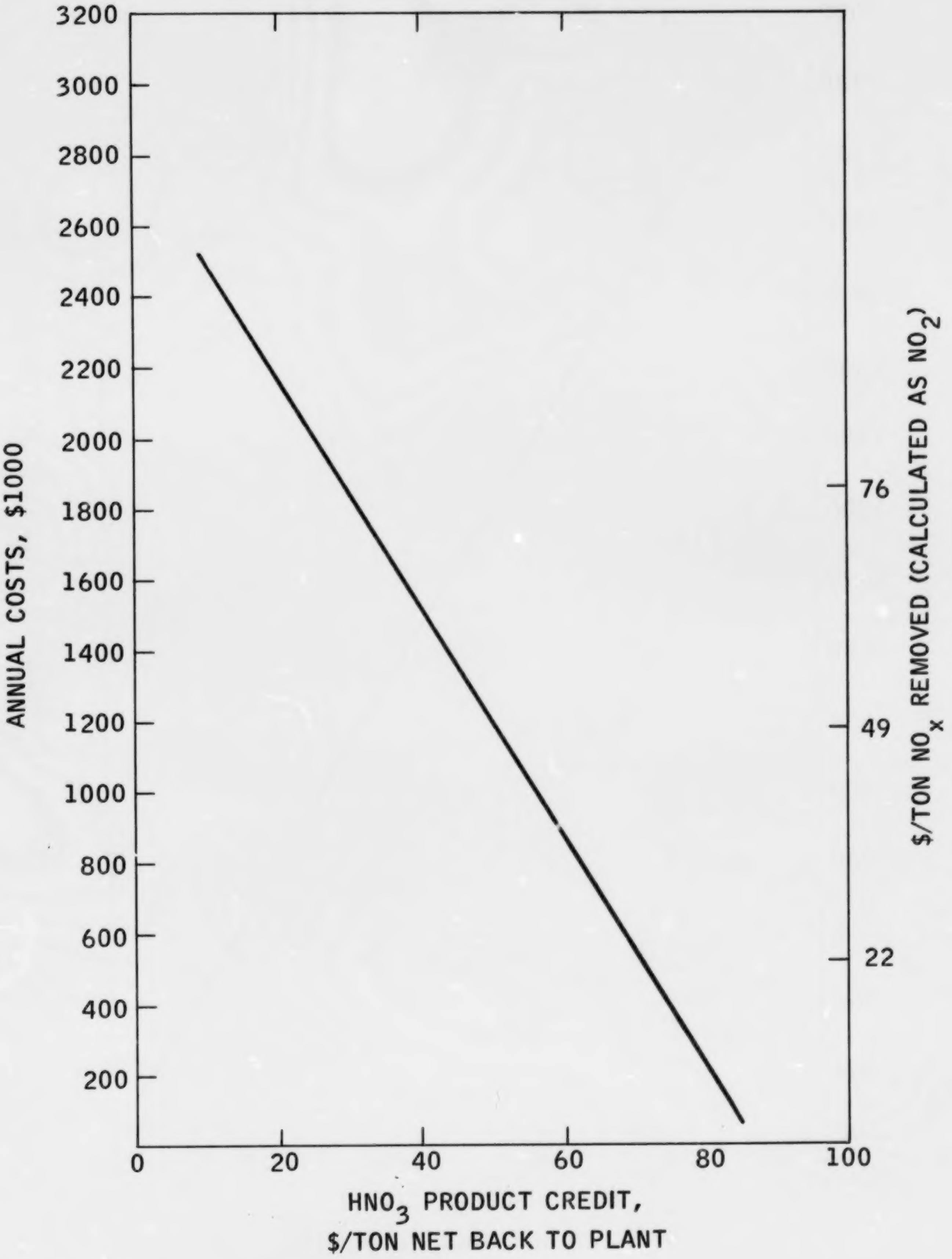
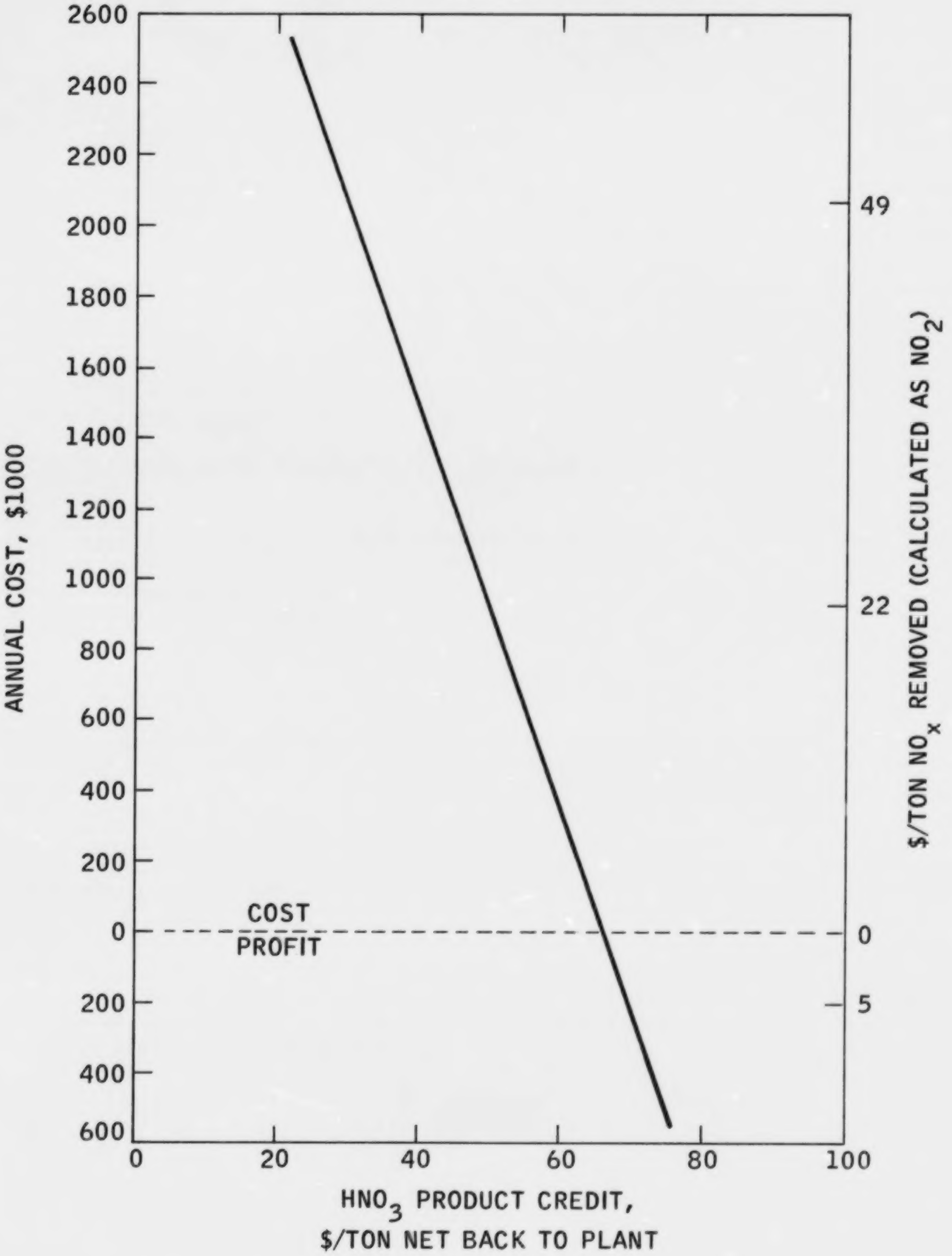


Figure 8-16E

SENSITIVITY OF CONTROL COSTS
TO BY-PRODUCT CREDITS -
SINGLE SCRUBBER LIMEWATER PROCESS
WITH THERMAL DECOMPOSITION
(1000 MW GAS-FIRED POWER PLANT)



A potential emission control process based on the use of $Mg(OH)_2$ scrubbing is shown in Figure 8-17. Once again, a spray tower and a single scrubber have been assumed to be sufficient for removing fly ash, sulfur and nitrogen oxides. A centrifuge has been selected for separating the nitrite solution from the unreacted $Mg(OH)_2$ and the $MgSO_3$ formed. The solids are transported to a fluidized bed reactor, where in contact with a hot combustion gas they are decomposed to yield MgO and a concentrated SO_2 containing gas which is converted to sulfuric acid. $Mg(NO_2)_2$ solution is decomposed under pressure at about 300°F to yield NO, MgO and a $Mg(NO_3)_2$ solution. Following addition of air, the NO is oxidized as in the limewater processes, but the HNO_3 produced is returned to the decomposer where it promotes the decomposition and yields additional $Mg(NO_3)_2$. Treatment of the $Mg(NO_3)_2$ solution with NH_3 then produces NH_4NO_3 and percipitates MgO. This MgO, together with that formed in the decomposition of the $MgSO_3$, is returned to the scrubber for reuse. Key assumptions made in the design of this process are:

- $MgSO_3$ (slightly soluble) is formed in the scrubber rather than $MgSO_4$ (very soluble) by keeping the solution alkaline and minimizing solids residence time in the scrubber.
- Decomposition of $MgSO_3$ at 1500°F is rapid and controlled by equilibrium.
- Costs of conventional sulfuric acid and ammonium nitrate plants are applicable to the modified system needed, e.g., cost of drying SO_2 containing gas from the $MgSO_3$ decomposer is equal to cost of melting and burning sulfur in a conventional plant.
- MgO make-up rate is 2% of the stoichiometric usage rate.

Investment and operating costs for the $Mg(OH)_2$ scrubbing system are given in Appendices 8-42 through 8-45 for 1000 MW coal and oil fired power plants and in Appendices 8-46 and 8-47 for a gas fired power plant of the same size. Costs were also calculated for 500 MW and 120 MW coal fired plants when it was found that the $Mg(OH)_2$ scrubbing system gave the lowest operating costs of all the flue gas treating processes. These costs are given in Appendices 8-48 and 8-49. Investment costs were calculated for these cases using a 0.7 scaling power applied to the investment cost calculated for the 1000 MW plants. A summary of control costs based on the standard operating and by-product credits (Table 8-16) appears in Table 8-18. Figures 8-17A, B and C show the sensitivity of control costs to changing ammonium nitrate and sulfuric acid by-product credits for 1000 MW power plants fired by coal, oil and gas, respectively.

Figure 8-17

SINGLE SCRUBBER $Mg(OH)_2$ CONTROL SYSTEM WITH THERMAL DECOMPOSITION

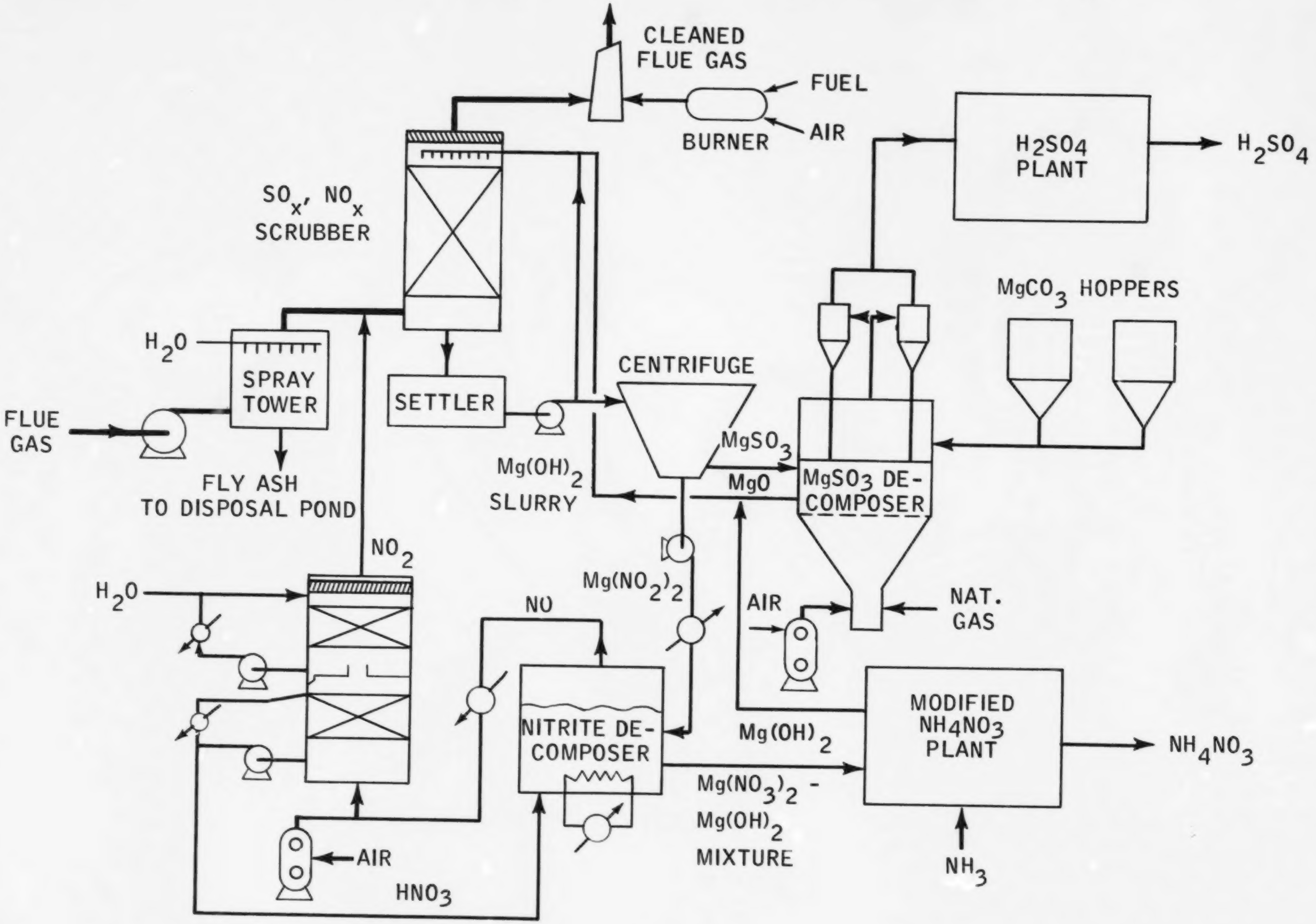

CLEANED FLUE GAS
FUEL
AIR
BURNER
H_2SO_4 PLANT
H_2SO_4
SO_x, NO_x SCRUBBER
$MgCO_3$ HOPPERS
H_2O
SPRAY TOWER
SETTLER
CENTRIFUGE
FLUE GAS
$MgSO_3$
$Mg(OH)_2$ SLURRY
MgO
$MgSO_3$ DE-COMPOSER
FLY ASH TO DISPOSAL POND
NO_2
$Mg(NO_2)_2$
H_2O
NO
AIR
NAT. GAS
MODIFIED NH_4NO_3 PLANT
NITRITE DE-COMPOSER
$Mg(OH)_2$
NH_4NO_3
$Mg(NO_3)_2$ - $Mg(OH)_2$ MIXTURE
AIR
HNO_3
NH_3

Figure 8-17A

SENSITIVITY OF CONTROL COSTS TO BY-PRODUCT CREDITS - SINGLE SCRUBBER $Mg(OH)_2$ PROCESS WITH THERMAL DECOMPOSITION (1000 MW COAL-FIRED POWER PLANTS)

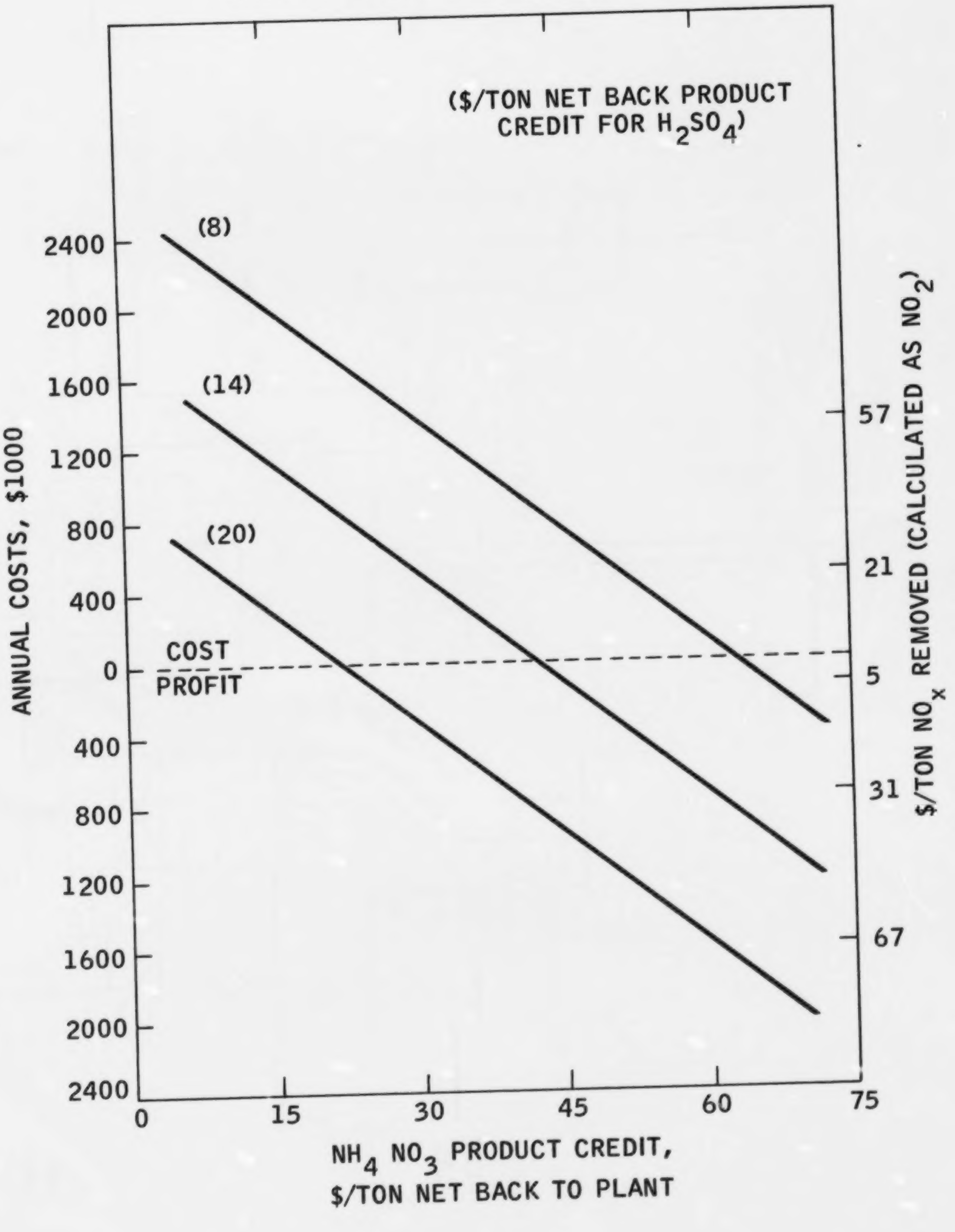


Figure 8-17B

SENSITIVITY OF CONTROL COSTS TO BY-PRODUCT CREDITS - SINGLE SCRUBBER $Mg(OH)_2$ PROCESS WITH THERMAL DECOMPOSITION (1000 MW OIL-FIRED POWER PLANT)

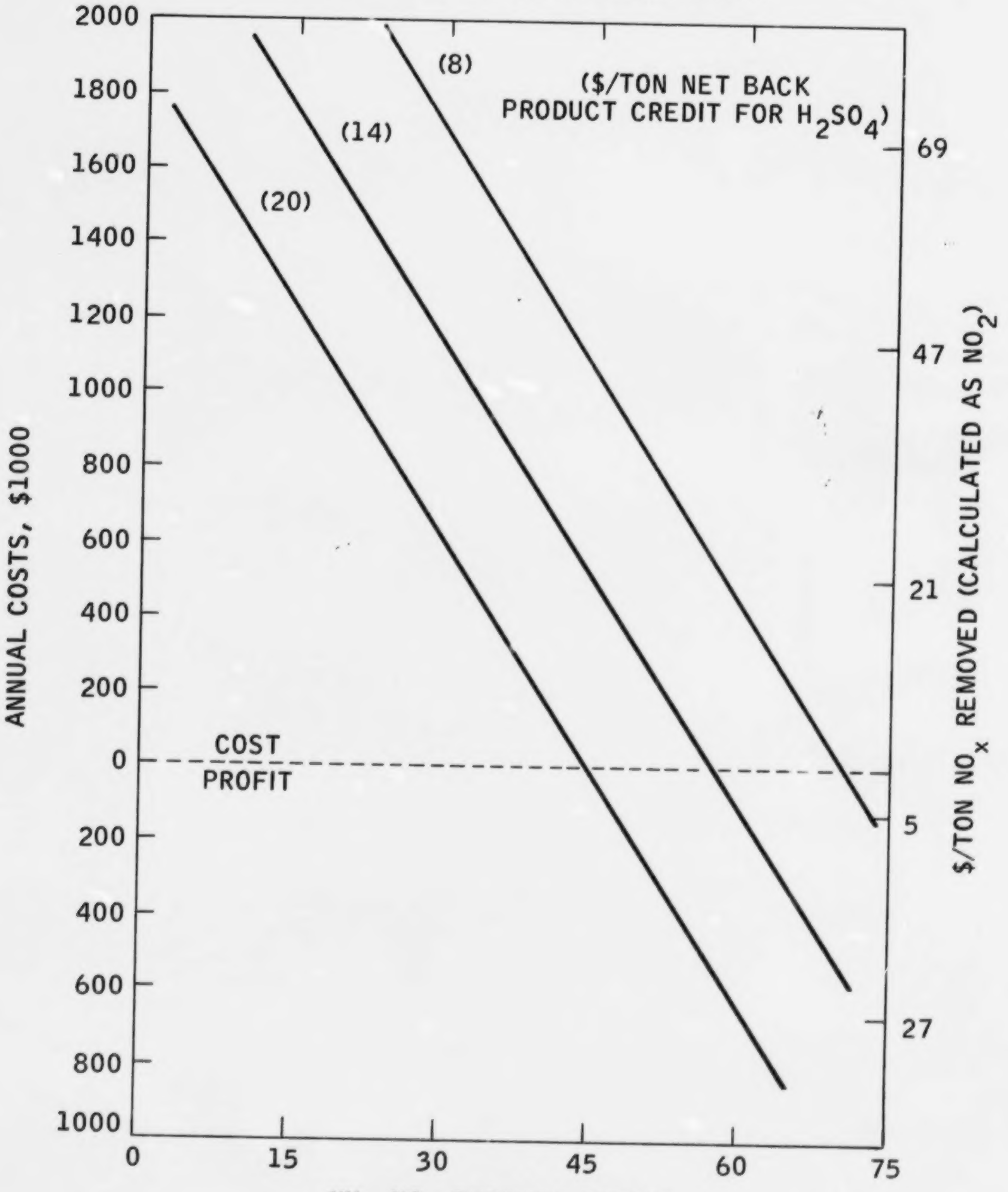


Figure 8-17C

SENSITIVITY OF CONTROL COSTS
TO BY-PRODUCT CREDIT -
SINGLE SCRUBBER $Mg(OH)_2$ PROCESS
WITH THERMAL DECOMPOSITION
(1000 MW GAS-FIRED POWER PLANT)

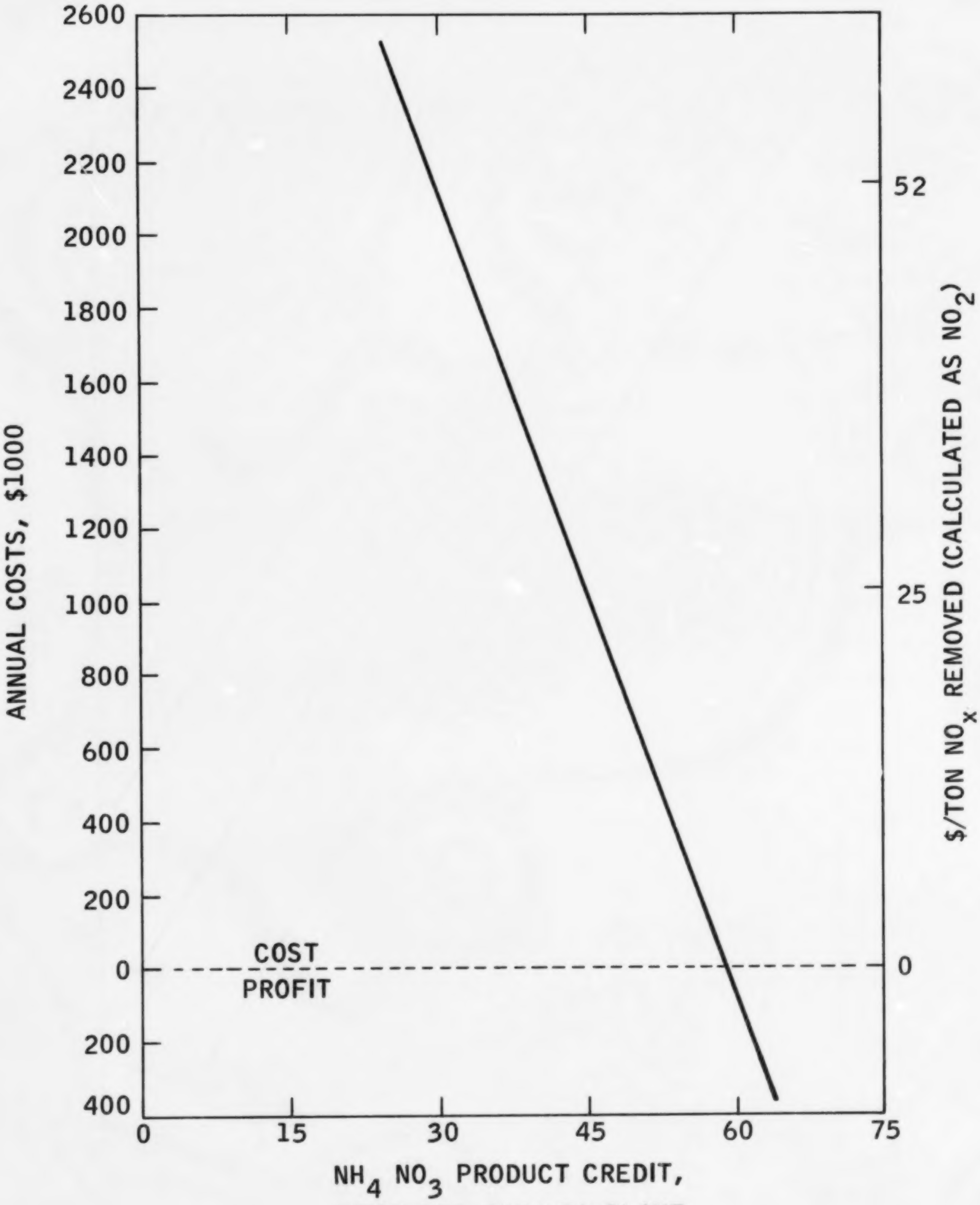


Table 8-18

Summary of Emission Control Costs
For 1000 MW Power Plant Using $Mg(OH)_2$ Scrubbing

Plant	Costs, $		
	Net Investment	Operating	
		Annual	$/Ton NOx Removed(1)
1000 MW Coal	12,000,000	(122,000) (profit)	(5.1) (profit)
1000 MW Oil	11,637,000	510,000	21
1000 MW Gas	10,455,000	1,039,000	25
500 MW Coal	7,400,000 (2)	398,000	39
120 MW Coal	2,712,000	528,000	530
750 MW Coal	--	--	10(3)

(1) Calculated as NO_2.
(2) Using .7 scaling power factor.
(3) Interpolated value from curve drawn through 1000 MW, 500 MW and 120 MW points.

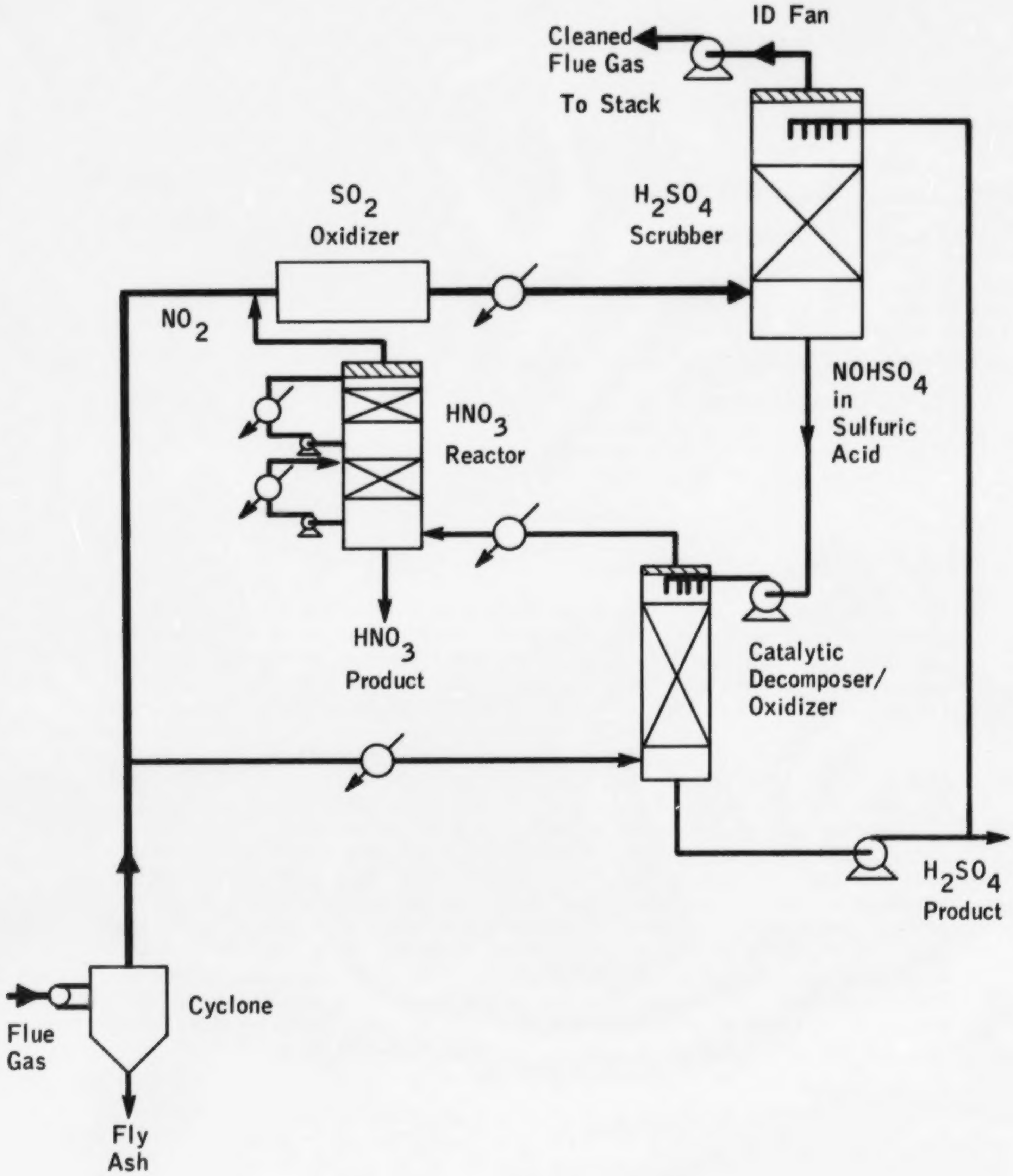
8.2.4 Sulfuric Acid Scrubbing

Based on an analysis of their two sulfuric acid scrubbing processes (see section 5.5.3) for sulfur and nitrogen oxides emission control, Tyco concluded that the isothermal process employing the catalytic decomposition-oxidation step offered the greater potential for low cost control (8-4). Our own analysis confirms this conclusion.

A flow diagram of the preferred Tyco process is shown in Figure 8-18. The process has been described in section 5.5.3 of the report. The main feature of the process is the recycle of sufficient NO_2 to the flue gas at 300°F to oxidize the SO_2 to sulfuric acid mist and provide an equimolar NO_2/NO ratio in the gas. The sulfuric acid mist and the nitrogen oxides are then absorbed in a very efficient scrubber. The scrubber operates isothermally at about 250°F with an 80% sulfuric acid solution. At this temperature and this acid strength, there is no net transfer of moisture between the flue gas and the acid. The spent acid is passed through a catalytic decomposer/oxidizer where the sulfuric acid-nitrogen oxides complex is decomposed by a portion of the flue gas into the acid and NO_2 for recycle to the flue gas and to product HNO_3. A portion of the untreated flue gas is used for the stripping.

Figure 8-18

TYCO'S ISOTHERMAL SULFURIC ACID SCRUBBING SYSTEM


ID Fan
Cleaned Flue Gas
To Stack
SO_2 Oxidizer
H_2SO_4 Scrubber
NO_2
$NOHSO_4$ in Sulfuric Acid
HNO_3 Reactor
HNO_3 Product
Catalytic Decomposer/ Oxidizer
H_2SO_4 Product
Cyclone
Flue Gas
Fly Ash

As already pointed out (section 5.5.3), because of the large NO_2 recycle requirements of the Tyco process, scubber efficiencies must be very high to obtain effective NO_x emission control. For design and cost calculations, scrubber efficiencies ranging from 92 to 98% have been assumed and costs have been developed as a function of these efficiencies. Other important assumptions that have been made in the analysis of this process are:

- Pressure drop through the high efficiency scrubbers is 10" H_2O. Pressure drop through ducts is 2" H_2O for a total of 12" H_2O.
- A char catalyst decomposes the acid-nitrogen oxides complex and provides nearly complete oxidation of NO to NO_2. Carbon loss is low and only the equivalent of one complete reactor charge must be added as make-up each year.
- Tyco's assumed acid sorption capacities of .055 gr. moles N_2O_3/liter acid are realized.

Breakdowns of investment and operating costs for Tyco's H_2SO_4 scrubbing process are given in Appendicies 8-50 through 8-53 for 1000 MW coal and oil fired plants and total operating costs based on the standard credits of Table 8-16 are shown in Figure 8-19 as a function of scrubber removal efficiency. Because of the nature of this process, equipment size is relatively insensitive to removal efficiencies. Therefore, a single plant investment has been assumed in costing the process. Based on an assumed scrubber efficiency of 95% (which may be optimistic), the sensitivity of control costs to changing nitric acid and sulfuric acid by-product credits are shown in Figures 8-19A and B for 1000 MW coal and oil fired power plants, respectively.

Figure 8-19

CONTROL COSTS FOR SULFURIC ACID SCRUBBING SYSTEM

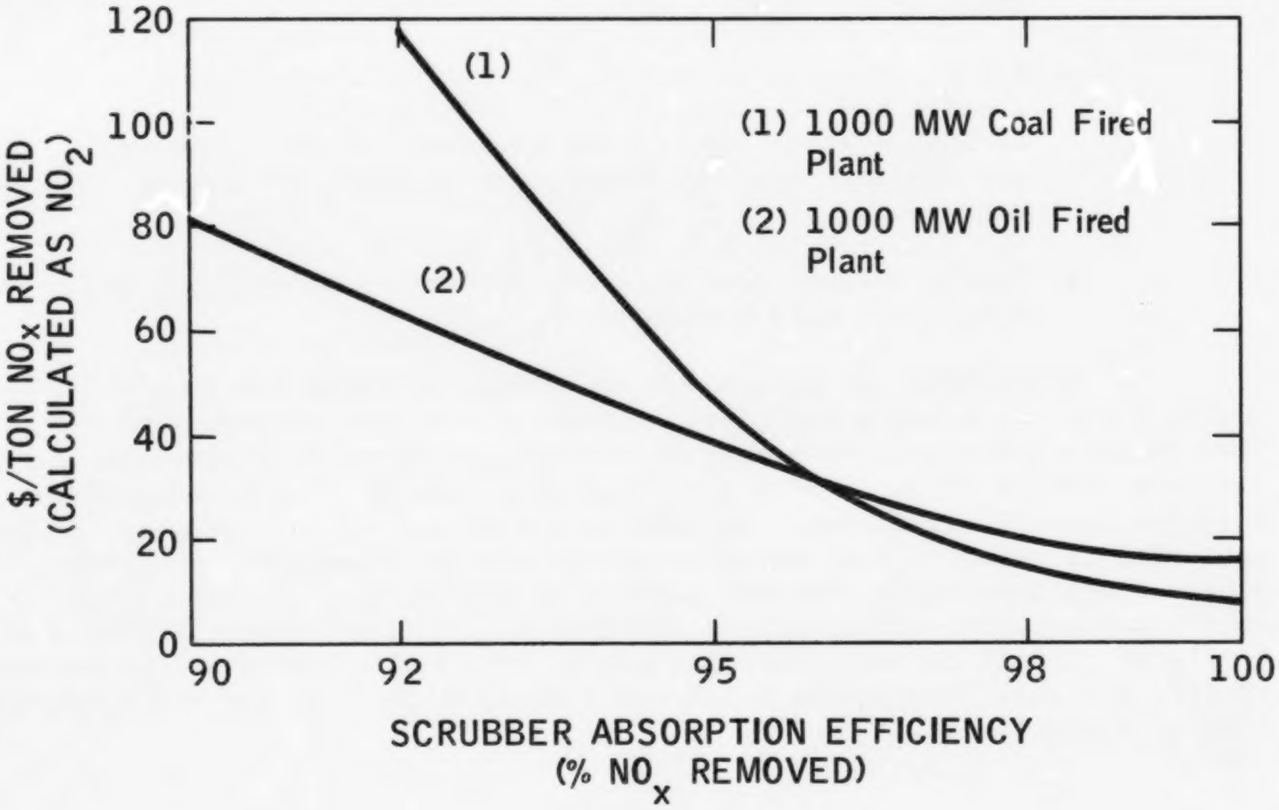


Figure 8-19A

SENSITIVITY OF CONTROL COSTS
TO BY-PRODUCT CREDITS
SULFURIC ACID SCRUBBING SYSTEM.
(1000 MW Coal-Fired Power Plant, 95% Scrubber Efficiency)

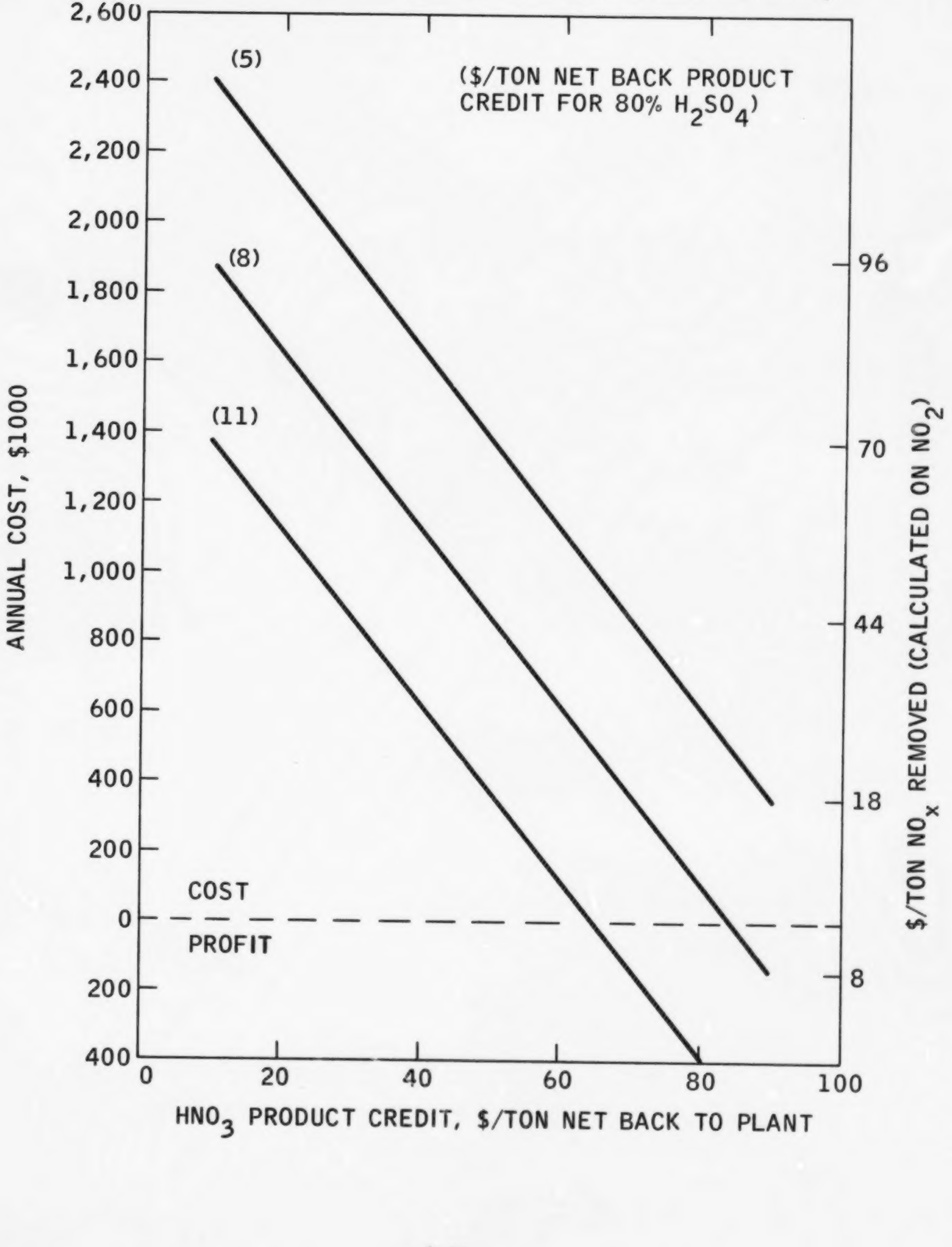
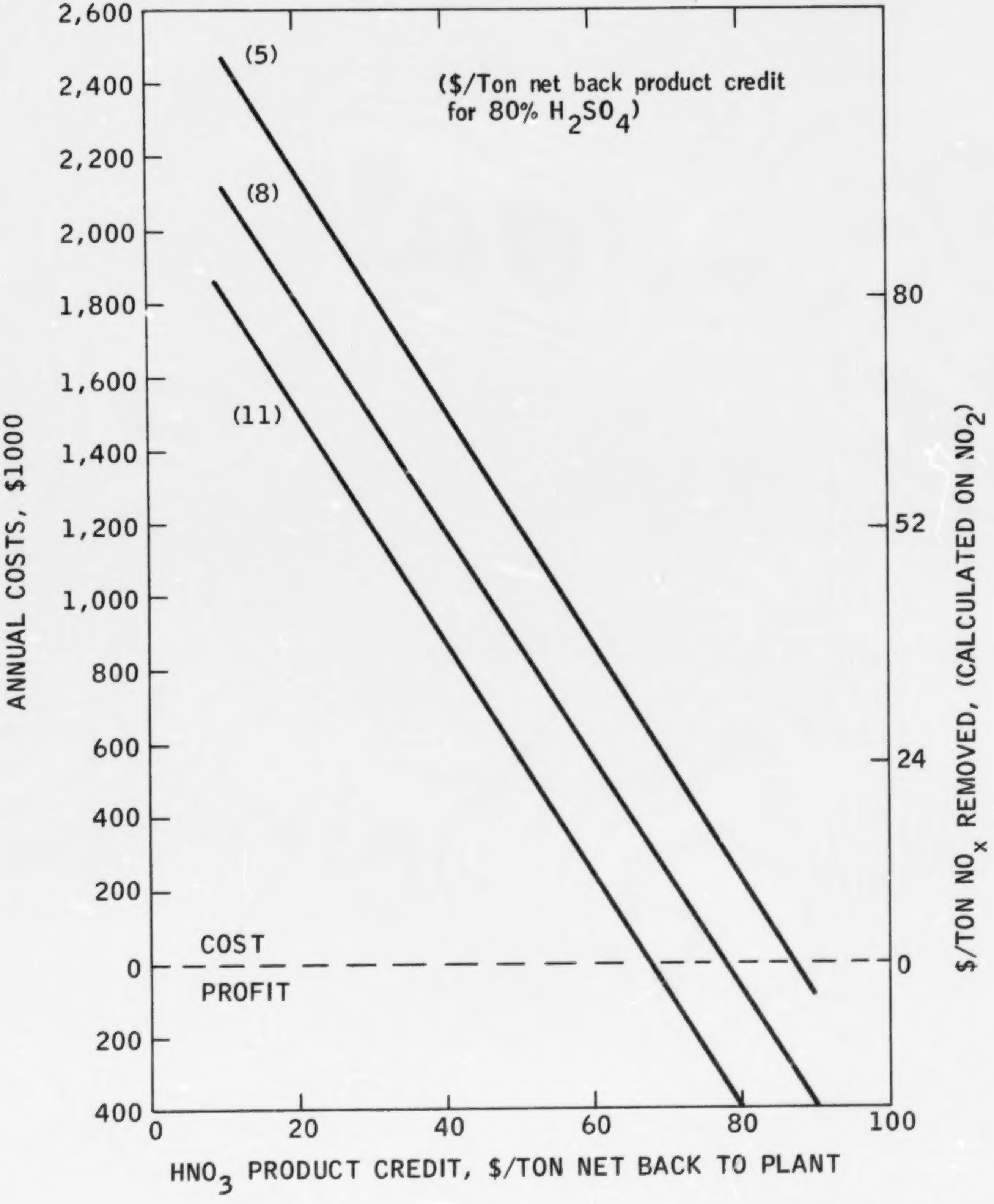


Figure 8-19B

SENSITIVITY OF CONTROL COSTS
TO BY-PRODUCT CREDITS
SULFURIC ACID SCRUBBING SYSTEM.
(1000 MW Oil-Fired Power Plant, 95% Scrubber Efficiency)



8.2.5 Summary of Combustion Flue Gas Treatment Control Costs

Table 8-19, shown below, summarizes the control costs for coal fired power plants using the flue gas treatment processes discussed in Section 8.2. The processes are listed in approximate order of increasing annual control costs. Clearly, absorption techniques are the most attractive of the flue gas treatment methods considered.

Table 8-19

Summary of Flue Gas Treatment Costs for Coal Fired Power Plants

Control Process	Investment, MM$	Operating Costs		
		$/Ton Coal	$/Ton NO_x	Mils/KWH
$Mg(OH)_2$ Scrubbing	12.0	-.06	-5	-0.02
H_2SO_4 Scrubbing:				
98% Scrubber Eff.	17.3	.17	14	0.06
92% Scrubber Eff.	17.3	.65	118	0.23
Limewater Scrubbing*	8.5	.50	45	0.18
NH_3 Reduction & Scrubbing**	15.0	.92	66	0.33
H_2S Reduction/Claus Process	11.7	.98	77	0.34
Selective H_2 Reduction**	4.1	1.02	81	0.36
Catalytic Decomposition**	4.1	.91	72	0.32

Basis: 1000 MW coal plant - 3% S coal
Flue gas desulfurization worth $.50/T coal

Standard Credits: S @ $25/T; H_2SO_4 @ $14/T (98%), $8/T (80%)
HNO_3 @ $50/T; NH_4NO_3 @ $45/T; $(NH_4)_2SO_4$ @ $20/T

* Single scrubber limewater control system with thermal regeneration of sorbent.
** Based on catalyst cost of $100/CF; space velocity 6000-7000 SCFH/CF.

8.3. TAIL GAS TREATMENT FOR NITRIC ACID MANUFACTURE AND USE

The following section discusses costs for control of NO_x in the manufacture of nitric acid, and in its use in organic oxidations and nitrations.

8.3.1. Nitric Acid Manufacture

By careful design and operation, some nitric acid manufacturers attain NO_x levels in untreated tail gas of 0.1 to 0.2% versus a typical level of 0.3% (8-5). The optimum level of NO_x in tail gas depends on the economic factors prevailing at each location: 0.1% reduction in NO_x means approximately 1% improvement in nitric acid recovery. The balance between the credits for improved recovery and the added cost for additional absorber stages, increased cooling, etc., determines the optimum level. This requires separate analyses at each installation.

Costs of emission controls may be partially offset by credits for products,or energy recovery. If NO_x can be removed from tail gas and recovered at high concentration, it may be returned as feed to the process. The value of the recovered NO_x is a potential credit for developing an absorption process. On the other hand, the cost of recovering dilute nitrate and nitrite salts in spent caustic may outweigh their product value. In catalytic reduction, all the products are released to the atmosphere, but the energy released in the reaction may be economically recovered in the turboexpander or waste heat boiler.

Costs for catalytic reduction will be affected by the type of treatment (non-selective decolorization or abatement, selective abatement, etc.), the volume of tail gas to be treated, the cost of fuel, and the value of the energy recovered.

In many situations, catalytic reduction for energy recovery and decolorization would be incorporated into the basic plant design, since the credits for energy recovery provide an acceptable return on the added investment. The investment for providing a full abatement system would be about 2% of the selling price of the unit, if designed into a new plant (8-6). This envisions successful operation of the two-stage system in which cool tail gas is used to quench partially reacted hot gas from the first stage (8-7), a system which eliminates the need for a heat exchanger (see section 6.1.1.).

Adding catalytic reduction to an existing unit is usually more difficult and costly than incorporating the facilities into a new unit as it is being designed. For existing plants, modifications to the heat exchanger train may be required to obtain and hold tail gas temperatures within the operable range. Physical space limitations may preclude placing the reactor ahead of the turboexpander. Additional preheat facilities would be required in placing the reactor after the turboexpander, and energy generated in the reduction would not be available for recovery in the turboexpander. For these reasons, costs of adding catalytic reduction to existing plants will vary with each application and will depend upon the modifications required for the installation.

Rough costs of three catalytic reduction alternatives have been derived in planning a new 300 T/D nitric acid plant. These alternatives are (1) decolorization, (2) single-stage selective abatement, and (3) two-stage non-selective abatement with a heat exchanger between stages. The comparison is shown below. The costs are strongly affected by conditions specific to the location, and therefore, these costs should not be used for general purposes.

Table 8-20

Estimated Costs of Catalytic Reduction

Case No.	(1)	(2)	(3)
Case No.	Decolorizer	Selective Abater	Two-stage Non-Selective Abater
NO_x before reduction, ppm	3000	3000	3000
NO_x after reduction, ppm	3000	300	300
Fuel	Nat. Gas	Ammonia	Nat. Gas
Investment, $1000	60	140	255
$ SCFM	2.60	6.10	11.00
Costs, $1000/Yr*			
Nat. Gas	14	--	82
Ammonia	--	33	--
Catalyst	4	12	8
Steam	(50)	(21)	(144)
Investment Based Costs**	30	70	128
Total Cost, $M/Yr	(2)	94	74
Total Cost, $/Ton HNO_3	(0.02)	0.95	0.75
Total Cost, $/Ton NO_x removed	--	34	27

* Parentheses indicate negative costs or savings.
** Includes 20% return before taxes.

In this comparison, investment for the abatement systems are two to four times the investment for decolorization. Selective abatement requires less investment than two-stage abatement. Overall operating costs, including 20% return before income taxes are approximately breakeven for decolorization. For most companies this corresponds to an after-tax return of 10% which is the current cost of capital. Operating costs for two-stage abatement are lower than for non-selective abatement, since steam credits more than offset higher investment and fuel costs.

In this plant, a turboexpander augmented by a steam turbine drives the compressor supplying air for oxidizing ammonia. Without catalytic reduction, tail gas would be preheated by exchange to a temperature 140°F below the limit for the turboexpander. In the decolorization alternative, fuel addition rate is set for the heat release to meet the temperature limit of the turboexpander. The additional power recovery at the expander is balanced by reducing steam to the turbine. In case 2, steam savings are smaller because the selective reduction provides only 60°F temperature rise. In case 3, additional steam savings are obtained by placing a waste heat boiler between stages, since only 140°F of the 680°F total temperature rise can be used in the turboexpander.

Investment based costs are assumed at 50% per annum including 20% return before income tax. Steam is credited at 75¢/thousand pounds; natural gas is charged at 40¢/M BTU and ammonia at $50/ton. Catalytic life was assumed to be 6 years for non-selective, and two years for selective operation, respectively.

To the extent that abatement is not yet completely satisfactory, the basis for this study has not been completely demonstrated.

In the mid-1950's a catalytic decolorizer was installed on a high pressure type nitric acid plant somewhat smaller than those referred to in Table 8-20 at a cost of $50,000. On the other hand, an estimate was recently made for a catalytic control device for a low pressure nitric acid plant of somewhat greater capacity than the plants in Table 8-20 This was to be a unit for decolorization or one-step, nonselective abatement, the choice depending upon the amount of synthesis gas ($3N_2 + H_2$) mixed with the tail gas. Estimated capital investment was $400,000. Operating cost per ton of nitric acid was estimated at $0.90 for decolorization and $2.30 for abatement (8-8).

Investments for catalytic reduction must provide for catalyst, reactor vessel, controls, and heat exchange equipment. Honeycomb catalyst costs about $2,000/cubic foot while spherical catalysts cost about $700/cubic foot (8-5). The costs per SCFM of tail gas are about equal, however, because honeycomb systems are designed for 100,000 SCFH of gas per CF of catalyst, while spherical catalyst systems are designed for space velocities of about 30,000 SCFH of gas per CF of catalyst. Thus, catalyst investments are about $1.20 per SCFM of tail gas or $100/T/D of nitric acid. If two catalyst stages are employed, the investment must be doubled.

Heat exchanger investments will range widely from a low of zero for equipping some new plants with decolorizers to about $85,000 for a waste heat boiler system in a 300 T/D nitric acid plant in a single-stage abator, and even higher costs for two-stage units employing heat exchangers.

Complete design and equipment lists are needed to obtain costs for any specific plant. In general, unit investment per pound per day of NO_x removal will vary inversely with plant size, placing the small plant at a cost disadvantage, relative to the large plant.

Operating costs must cover the cost of fuel, repair labor and materials, catalyst replacement, and capital charges. Fuel costs are location dependent and also vary with the type of fuel burned. Usually natural gas is less expensive than hydrogen, because costs per MSCF are about the same and only 25% as much is required. Hydrogen costs may approach the cost of methane when waste hydrogen is available, but the amount available from ammonia manufacture would usually be adequate only for decolorization. The supply will not be available during the ammonia plant shutdowns.

Costs were not developed for caustic scrubbing because disposal of spent caustic solution prohibits use of this method at most locations. An estimate of the cost of adding a two-stage abator to an existing plant has been given by Decker (8-9), as ranging from about $750 to $1125 per ton per day of nitric acid capacity for abatement, corresponding to that shown, in Table 8-20. The abator is installed after the turbine, so that there is no credit for energy recovery. This operation is said to require fuel costs of 50¢ per ton of HNO_3.

8.3.2. Organic Oxidations and Nitrations

The economics require recovery of nitric acid from the reactor off-gas in large scale organic oxidations using nitric acid as the oxidizing agent. For example, the incentive for acid recovery for a 100 million pound per year adipic acid plant would be about $1.6 million/year. This figure is based on recovering 0.3 pounds of HNO_3/pound of adipic acid and a nitric acid cost of $3.90/100 pounds (8-11). The optimum economic recovery level is subject to economic analysis at each installation. Similarly, in large scale nitrations, recovery of nitric acid by absorbing concentrated NO_x emissions should be economical.

When additional NO_x abatement is required, fume incineration is often used. Fume incinerator investments are quoted at $10,000 to $20,000 by one source (8-11). Another suggests investments of $75,000-$150,000 to install flame abatement facilities for existing small batch nitrators and $75,000-$250,000 for existing large nitrators. Annual operating costs were estimated at $25-85 thousand per product for small batch nitrators and $25-40 thousand for continuous nitrators (8-10).

8.4. STATIONARY ENGINES

Little information is available on costs of reducing NO_x from stationary engines. The following brief discussion will cover diesel and gas engines.

8.4.1. Diesel Engines

Currently, the only effective way to reduce NO_x is to use engines with design features which tend to minimize NO_x production (see Section 4.5.). Engines employing precombustion chambers, which minimize NO_x, may have slightly higher initial costs and fuel consumption than engines without precombustion chambers. The magnitude of the cost differential would have to be established by obtaining price quotations for specific applications.

8.4.2. Gas Engines

Reduction in NO_x by increasing air/fuel ratio from the optimum power setting decreases power output by as much as 30%. This would, in turn, increase original engine costs by as much as 30%.

Water injection into the intake manifold of gas engines has promising potential for NO_x removal. The initial cost of a system for water injection was roughly estimated at $2000 per engine. With water costs of 20¢/thousand gallons, the costs of reducing NO_x emissions would be:

Table 8-21

NO_x Control Costs for Stationary Gas Engines

Engine HP	80	800	4200
Cost, $/yr.	60	800	930
Cost, $/ton NO_x eliminated	420	9.30	1.20

The numbers show very high costs per unit of NO_x removed for small engines, and low costs for large engines. The costs are based on 20% capital charges, an injection rate of 1.25 lbs. water/lb. fuel, and 75% reduction in NO_x.

8.5 Summary

Detailed cost data development for all sectors considered in this study are given in the Appendix. The cost-effectiveness assessment of economically attractive control methods in Section 9 is based on the combination of cost evaluations with the estimated control level of NO_x emissions.

8.6 REFERENCES

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(8-2) Monsanto: Removing SO_2 Pollutant From Flue Gas. Chemical Engineering, 76 (26):88-9, 1969.

(8-3) Sulfur Oxide Removal From Power Plant Stack Gas: Use of Limestone in Wet Scrubbing Process. Report prepared by TVA for NAPCA Under Contract TV-29233A.

(8-4) Tyco Modified Chamber Process for Removal of SO_2 from Power Plant Flue Gas. Presented at Second Semi-Annual Control Process Contractors Meeting sponsored by NAPCA, Cincinnati, Ohio, June 11-13, 1969.

(8-5) Private communications with catalyst and chemical companies.

(8-6) Letter from D. J. Newman, Chemical Construction Corp., to A. R. Cunningham, Sept. 17, 1969.

(8-7) Newman, D. J. and Klein, L. A., "Apparatus for Exothermic Catalytic Reactions," U.S. 3,443,910, Filed June 30, 1966.

(8-8) Letter from J. L. Parsons, E. I. duPont de Nemours & Co. to D. L. Waters, NAPCA, October 10, 1969.

(8-9) Decker, L. D., "Incineration Techniques for Controlling Emissions of Nitrogen Oxides," APCA Preprint No. 67-148.

(8-10) Private communications, E. I. duPont de Nemours & Co., March 1969.

(8-11) Oil, Paint, and Drug Reporter, April 21, 1969.

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9. COST EFFECTIVENESS ANALYSIS OF NO_x CONTROL METHODS APPLIED TO COMBUSTION SOURCES

The major objective of performing a cost effectiveness analysis is to provide a relevant basis for establishing priority ratings for research and development projects involving potentially useful NO_x control technology. The data developed in this analysis are also useful in assessing the magnitude of the NO_x emissions problem by considering various levels of success in control method research and subsequent application to combustion sources.

Since this analysis is rather complex when applied to all major United States stationary NO_x sources, a series of applications will be made starting with a simple case and proceeding logically to more comprehensive cases. Thus, analysis is first applied to single power boilers, then to a full power plant, next to all power plants in two large industrial urban regions, then to all United States fossil fuel steam electric plants and finally to all major combustion sources in the United States. In this manner, the methodology, sources of data, and assumptions can be readily highlighted without excessive detail.

As illustrated in the following sections, the major NO_x emitting sources have been classified into a minimum number of groups that differ significantly in one or more of the following factors: source type, size, load factor (operating hours per year), average emission rate, type of fuel burned, cost of control and effectiveness of control (% reduction of NO_x emissions).

The cost effectiveness (C/E) for each potential control method applied to a particular combustion source is defined as the ratio of (1) annual dollar cost of control to (2) annual reduction of NO_x emission in tons, calculated as NO_2. Generally, (C/E) is calculated as follows:

$$C/E = \frac{\$\ \text{Control Cost/Year}}{(\text{Fuel Used/Hour})\ (\text{Hours/Year})\ (\text{Em. Factor})\ (\%\ \text{Control Effectiveness})}$$

Control cost in this calculation includes both fixed costs and operating costs. Since very little actual NO_x control has been applied, it has been necessary to estimate the costs and effectiveness of potential control methods based on theory and engineering judgement when extrapolation from demonstrated methods was not practical. Thus a range of uncertainty exists for each element of the analyses.

The time period selected to define the NO_x problem is another important factor in making these studies. Since cost effectiveness analysis is a tool to guide research and development plans which take time to develop and implement, it is necessary to define the pollution problem for a time period in the future. For example, the period 1975-1985 can be defined fairly accurately from projections of past trends since technological and economic changes will probably be relatively minor in this time period, compared to a more distant period such as 1985-2000. Accumulating the emissions over the entire period selected might give a slightly better definition of the pollution problem,than selecting a single representative year. However, this added complexity is probably not warranted in view of the degree of uncertainty in each of the values used in calculating cost effectiveness ratios. In addition, selecting a year such as 1980 to represent the problem has several advantages. NO_x emissions forecasts have been made for 1980 and there are many forecasts available for comparison. 1980 is near enough in the future to represent a realistic problem,and the results of research and development could be applied by that year. In addition, the problem of estimating the population distribution of emission sources by size, type of fuel burned, etc., is greatly simplified by selecting a typical year, rather than a span covering many years. Based on these considerations, we have selected the year 1980 to represent the target period aimed at in the cost effectiveness analysis which follows.

It should be emphasized that an important consideration in developing accurate cost effectiveness analysis is to estimate the appropriate emission factors to use for each class of emitting source in the future, say the year 1980. For example, what will the average emission factor for 750 MW gas fired boilers be in the year 1980? Will the 100-150 ppm currently achieved at one plant represent an United States average, or will 300 or perhaps 50 ppm be more realistic as compared to the 1500 ppm experienced initially? Due to lack of sufficient emission measurements, similar problems exist in establishing an accurate basis for the very large coal burning boilers which will exist in the year 1980. Where available, representative emission rates determined from actual tests were used. For other sources with known heat rates, Los Angeles Joint Study (9-1) curves were applied. Finally, Public Health Service (9-2) and other emission factors found in the literature were used when necessary.

It is also important to note that in some cases cost estimates have been based on retrofitting existing units. Experience gained at a West Coast power station indicates that "short-cut" methods may be applicable, resulting in low costs for NO_x control. These aspects of the problem will also be discussed further in the cases that follow.

9.1 COST EFFECTIVENESS PROFILES FOR A LARGE GAS AND OIL FIRED POWER PLANT

Table 9-1, lists basic data on ten steam boilers installed in one of the generating stations of a large electric utility company. These data were obtained from a Steam-Electric Questionnaire, from information supplied by the National Air Pollution Control Administration and from private communications. Cost effectiveness analysis for combustion control using these data will be applied, first to a 750 megawatt capacity boiler, then to a 120 megawatt capacity boiler and finally, cost effectiveness profiles will be constructed for the entire plant. The results obtained will then be contrasted with the results calculated from alternate costs and emission factors to indicate how sensitive the results are to alternate assumptions.

TABLE 9-1

BOILER DATA FOR ELECTRIC GENERATION PLANT SELECTED AS EXAMPLE

Boiler Information	Boilers 1-6	Boilers 7,8	Boilers 9,10
Capacity Rating - MW	80	120	750
Max. Cont. Rat. 10^3 lb/Hr.	600	850	5300
Type of Firing	Fr. Wall	Fr. Wall	Hor. Op.
Initial of Year of Oper.	1950,'51	1952	1967,'68
Flue Gas Rate: Oil (10^3 Lbs/Hr.)	652	1110	5558
Gas	646	1100	5564
Excess Air: Oil	15%	15%	10%
Gas	10%	5%	5%
NO_x Emis. - ppm: Oil (Uncontrolled)	473	550	400
Gas	335	377	1500
Manufacturer	B&W	B&W	B&W
Plant Fuel Consumption-1967 Oil	937,000 Bbl or 6 x 10^{12} BTU		
Plant Fuel Consumption-1967 Gas	20 x 10^9 Cu. Ft. or 22 x 10^{12} BTU		

Tables 9-2 and 9-3 summarize estimated costs for five NO_x combustion modification control methods. These costs are then used in Tables 9-4 and 9-5 together with estimates of NO_x emissions and control method effectiveness to develop estimated annual costs per ton of NO_x removed by each of the five control methods considered.

The costs estimated on Table 9-2 are based upon a large gas or oil fired boiler supplying steam for a 750 megawatt capacity turbine-generator. Although this size boiler is among the largest gas or oil fired boiler in use today, it will probably represent an average sized unit in the year 1980. The plant represented in Table 9-1 contains two new units of this size which have successfully reduced NO_x emissions through combustion modification. Information on this plant's NO_x emissions were obtained through NAPCA. These data, plus steam boiler operating data from our questionnaire, and estimated costs developed in consultations with Babcock and Wilcox Company have enabled us to estimate cost effectiveness by combustion control on a reasonable basis.

TABLE 9-2

ESTIMATED NO_x CONTROL COSTS - 750 MW STEAM BOILER

Control Method	Fixed Costs			Operating Costs			Total Costs per Year $1,000	
	Start-up Costs $1,000	Capital Equipment Costs $1,000	Capital Charges $1,000	Maintenance Supplies & Overhead $1,000	Other Operating Costs $1,000			
	(1)	(2)	(3)	(4)	(5)		(6)	
			14% of $\frac{(1)}{2}$ + (2)****	x% of (2)****			(3) + (4) + (5)	
					Gas	Oil	Gas	Oil
1. Low Excess Air	2.5 (25 man-days)	Instr. 100	14	(17.3%) 17	(111)*	(216)*	(80)	(185)
2. Modified Two-Stage Combustion	1.5 (15 man-days)	0	0	0	0	0	0	0
3. Flue Gas Recirculation	2.5 (25 man-days)	492	69	(8.63%) 42	38**	38**	149	149
4. Water Injection	0.5 (5 man-days)	18	3	(8.63%) 2	111***	108***	116	113

* Based on 1% reduction in gas fuel or 2% reduction in oil fuel.
For gas: 0.01 x 6 x 10^6 ft^3/hr x 5600 hrs x 1090 BTU/ft^3 x $0.303/$10^6$ BTU = $111,000/year savings.
For oil: 0.02 x 1000 bbl/hr x 5600 hrs x 18,000 BTU/lb x 342 lbs/bbl x $0.314/$10^6$ BTU = $216,000/year.

** Based on blower of 2.4 hp/MW. ∴ 2.4 x 750 x .746 watt/hp x $.005/KWH x 5600 hr = $38,000/year.

*** Maximum water injection economically feasible is 1% fuel loss.

**** Per NAPCA guidelines as described in the text.

NAPCA guidelines were used in estimating capital charges and operating costs. Capital charges have been estimated on the basis of 14% of investment costs. Maintenance costs have been estimated as 10% of instrument investment, 5% of investment for equipment having moving parts (such as fans, pumps, etc.) and 1% of investment for equipment having no moving parts (such as ductwork, isolating partitions etc.). Supply costs were estimated as 15% of maintenance costs. Plant overhead was estimated at 50% of maintenance and supplies. Other operating costs have been estimated as indicated in the footnotes of Tables 9-2 and 9-3. Gas and oil BTU content and costs per 10^6 BTU were obtained from Steam Electric Plant Factors/1968 edition (9-3).

Equipment costs for low excess air and modified two-stage combustion have been reduced in line with actual experience at this plant. No equipment modifications were required to achieve NO_x emission reductions at this station. Operating modifications were made with existing personnel apparently at no additional cost. We have applied a small manpower requirement and some instrumentation which may be required in the future. We must caution that not all gas and oil fired boilers will be capable of achieving low NO_x operation without significant investment costs.

Tables 9-4 and 9-5 contain the estimated control costs per ton of NO_x reduction based on the cost data from Tables 9-2 and 9-3. NO_x emissions were calculated from measured flue gas rates and emission factors.

Low excess air (1% oxygen in flue gas) reduced NO_x emissions about one-third on gas or oil fired boilers. Reduced costs are due to increased boiler efficiency of about 1%. "Modified" two-stage combustion in combination with low excess air reduced NO_x emissions by over 90% on the 750 MW gas fired boilers accompanied by a cost reduction of $2.31 for each of the 34,675 tons NO_x reduction per year.

Modified two-stage combustion has involved no additional construction cost. Less than stoichiometric quantities of air enter the lower burners of a port with only air used in the top burner of a port. Thus, the furnace volume supplied by the top row of burners acts as a modified second stage of combustion.

Table 9-5 contains estimated control costs per ton of NO_x reduction for a 120 MW boiler calculated in the same manner as Table 9-4. According to the data in Table 9-1, oil-firing results in higher NO_x emissions than gas firing. Thus the cost effectiveness figures are lower for oil firing than for gas firing.

TABLE 9-3

ESTIMATED NO_x CONTROL COSTS - 120 MW STEAM BOILER

Control Method	Fixed Costs: Start-up Costs $1,000	Fixed Costs: Capital Equipment Costs $1,000	Fixed Costs: Capital Charges $1,000	Operating Costs: Maint. Supplies & Overhead $1,000	Operating Costs: Other Operating Costs $1,000		Total Costs per Year $1,000	
	(1)	(2)	(3)	(4)	(5)		(6)	
			14% of $\frac{(1)}{2}$+(2)****	x% of (2)****			(3) + (4) + (5)	
					Gas	Oil	Gas	Oil
1. Low Excess Air	2.5 (25 man-days)	Equip. 0 Instr. 25 25	4	17.3% $4.3	(17)*	(33)*	(8.7)	(24.7)
2. Modified Two-Stage Combustion	1.5 (15 man-days)	0	0	0	0	0	0	0
3. Flue Gas Recirculation	2.5 (25 man-days)	118	17	8.63% $10.2	5**	5**	32.2	32.2
4. Water Injection	0.5 (5 man-days)	4	1	8.63% $0.3	17**	17**	18.3	18.3

* 1% reduction in gas fuel, 2% reduction in oil fuel.

For gas firing 0.01 x 1.2 x 10^6 ft^3/hr x 4300 hrs x 1090 BTU/ft^3 x $0.303/$10^6$ BTU = $17,000.

For oil firing 0.02 x 200 bbl/hr x 4300 hrs x 18,000 BTU/lb x 342 lbs/bbl x 0.314/10^6 BTU = $33,000/yr.

** Blower consumption = 2.4 hp/MW based on 15% flue gas recycle.

*** Maximum water injection economically feasible is equivalent to 1% fuel loss.

Cost = 1% of annual fuel costs.

**** Per NAPCA guidelines as described in the text.

TABLE 9-4

ESTIMATED CONTROL COSTS PER TON OF NO_x REDUCED - 750 MW BOILER

Control Method (% NO_x Reduction)	Gas Fired			Oil Fired		
	Total Control Costs per Year $1,000 *	NO_x Reduction per Year Tons	Control Costs $/Ton	Total Control Costs per Year $1,000	NO_x Reduction/Yr Tons	Control Costs $/Ton
1. No Controls (0% NO_x Reduction)	0	(38,528)**	--	0	(9,773)**	--
2. Low Excess Air (33% Gas; 33% Oil)	(80)	12,714	(6.29)	(185)	3,225	(57.36)
3. Two-Stage Combustion (50% Gas; 40% Oil)	0	19,264	0	0	3,909	0
4. Gas Recirculation (33% Gas; 33% Oil)	149	12,714	11.72	149	3,225	46.20
5. Water Injection (10% on Gas or Oil)	116	3,853	30.11	113	977	115.66
6. Low Excess Air + Two-Stage Combustion (90% Gas; 73% Oil)	(80)	34,675	(2.31)	(185)	7,134	(25.93)

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* From Table 9-2.

** Tons NO_x emitted per year calculated from measured flue gas rates and NO_x emissions.

For gas: $$\frac{(5.564)\ (10^6\ \text{lbs. flue gas/hr.})\ (1500\ \text{ppm})\ (46\ \text{lbs./mole})\ (5600\ \text{hrs./year})}{(27.9\ \text{lbs./mole})\ (2000\ \text{lbs./ton})} = 38{,}528\ \text{tons } NO_x \text{ per yr.}$$

TABLE 9-5

ESTIMATED CONTROL COSTS PER TON OF NO_x REDUCED - 120 MW BOILER

Control Method (% NO_x Reduction)	Gas Fired: Total Control Costs per Year $1,000*	Gas Fired: NO_x Reduction per Year Tons	Gas Fired: Control Costs $/Ton	Oil Fired: Total Control Costs per Year $1,000	Oil Fired: NO_x Reduction/Yr Tons	Oil Fired: Control Costs $/Ton
1. No Controls (0% NO_x Reduction)	0	(1,552)**	--	--	(2,061)**	--
2. Low Excess Air (33% Gas; 30% Oil)	(8.7)	512	(16.29)	(24.7)	618	(39.97)
3. Modified Two-Stage Combustion (40% Gas; 30% Oil)	0	621	--	0	618	--
4. Gas Recirculation (25% Gas; 30% Oil)	32.2	388	82.99	32.2	618	88.83
5. Water Injection (10% on Gas or Oil)	18.3	155	118.06	18.3	206	88.83
6. Low Excess Air + Two-Stage Combustion (66% Gas; 60% on Oil)	(8.7)	1,024	(8.50)	(24.7)	1,237	(19.97)

* From Table 9-3.

** Tons NO_x emitted per year calculated from measured flue gas rates and NO_x emissions: Thus for gas

$$\frac{(1.1 \times 10^6 \text{ lbs. flue gas/hr}) \; (377 \text{ ppm NOx}) \; (19 \text{ lbs./mole}) \; (4300 \text{ hrs./yr.})}{(27.9 \text{ lbs./mole}) \qquad (2000 \text{ lbs./ton})} = 1552 \text{ tons } NO_x\text{/yr.}$$

Table 9-6 summarizes the estimated control costs for the entire station of 10 boilers based on 21% oil and 79% gas firing.

Figure 9-1 presents the data from Table 9-6 in graphical form. The horizontal scale indicates control effectiveness in thousands of tons of NO_x reductions per year. The maximum emission is 73,154 tons of NO_x per year on a totally uncontrolled basis. Negative costs or credits reflect the annual operating savings inherent with the low excess air control method. For a gas-fired unit, this is estimated as 1% of the annual fuel costs based on an improvement in efficiency. Oil fired units include the same improvement plus decreased costs due to improvements in slagging and reduced high and low temperature corrosion.

The cost-effectiveness profiles may be analyzed as follows. The solid line labeled "low excess air" indicates a reduction in NO_x emissions of 24 thousand tons per year, at a saving of $275,000 per year in the operation of the plant. Low excess air plus "modified" two-stage combustion, as practiced at this plant, result in a reduction of 63 thousand tons of NO_x emissions per year, a reduction of 85%. Adding gas recirculation and water injection are estimated to result in a minor reduction of emissions, at very high incremental costs. The technical feasibility of adding gas recirculation and water injection in combination with low excess air and modified two-stage combustion remains to be demonstrated. The dashed lines indicate other routes which might be considered. Visual inspection indicates, that for this plant, low excess air plus "modified two-stage combustion" is the most cost-effective route for NO_x reductions of 63 thousand tons or less.

The sensitivity of the estimated control costs per ton NO_x reduction to alternate emission rate assumptions are shown below in Tables 9-7 and 9-8. Thus, for the very large, uncontrolled (750 MW) boiler, 38,528 tons of NO_x would be emitted per year based on measured emission rates on that unit. Calculating NO_x emissions based on actual heat release and extrapolation of the Los Angeles emission curves, this boiler would emit only 8,460 tons of NO_x per year. Applying the expected % NO_x reduction for each control method to these uncontrolled amounts gives the expected number of tons of NO_x reduced per year. Application of the costs developed in Table 9-2 to these two sets of NO_x reductions produces widely differing cost-effectiveness ratios. The ratios calculated from measured emission rates are undoubtedly more accurate for the boilers of this plant. However, the most representative values for other plants can only be accurately obtained from actual measurements.

Table 9-8 has been calculated on the same basis as Table 9-7 for a 120 MW boiler. In this case, use of the alternate emission rates yields almost identical results for oil firing but fairly wide

TABLE 9-6

ESTIMATED NO_x CONTROL COSTS FOR ELECTRIC GENERATION PLANT SELECTED AS EXAMPLE

Control Method	Costs per Year - $1,000					NO_x Reduction/Yr - Tons				Plant Total*	Control Cost $/Ton NO_x
	6 Boilers 80 MW**	2 Boilers 120 MW	2 Boilers 750 MW	Subt.	Plant* Total	6 Boilers 80 MW	2 Boilers 120 MW	2 Boilers 750 MW	Subtotal		
1. No Control, Oil	--	--	--	--		6,133	4,122	19,546	6,258	73,154	--
Gas						4,518	3,104	77,056	66,896		
2. Low Excess Air											
Oil	(98)	(49)	(370)	(517)	(275)	1,840	1,236	6,450	9,526	24,085	--
Gas	(34)	(17)	(160)	(211)		1,504	1,024	25,428	27,956		
3. Modified Two-Stage Combustion											
Oil	0	0	0	0	0	1,840	1,236	7,818	10,894	35,134	--
Gas	0	0	0	0		1,807	1,242	38,528	41,577		
4. Gas Recirculation											
Oil	128	64	298	490	490	1,840	1,236	6,450	9,526	23,593	20.77
Gas	128	64	298	490		1,130	776	25,428	27,334		
5. Water Injection											
Oil	74	37	226	337	342	613	412	1,954	2,979	7,310	46.79
Gas	74	37	232	343		452	310	7,706	8,468		
6. Low Excess Air + Modified Two-Stage Combustion											
Oil	(98)	(49)	(370)	(517)	(275)	3,680	2,472	14,268	20,420	62,669	--
Gas	(34)	(17)	(160)	(211)		2,982	2,048	69,350	74,380		

* 21% oil, 79% gas fired.

** Cost estimated as 2 times cost for two - 120 MW units.

Figure 9-1

COST-EFFECTIVENESS PROFILES
WEST COAST POWER PLANT

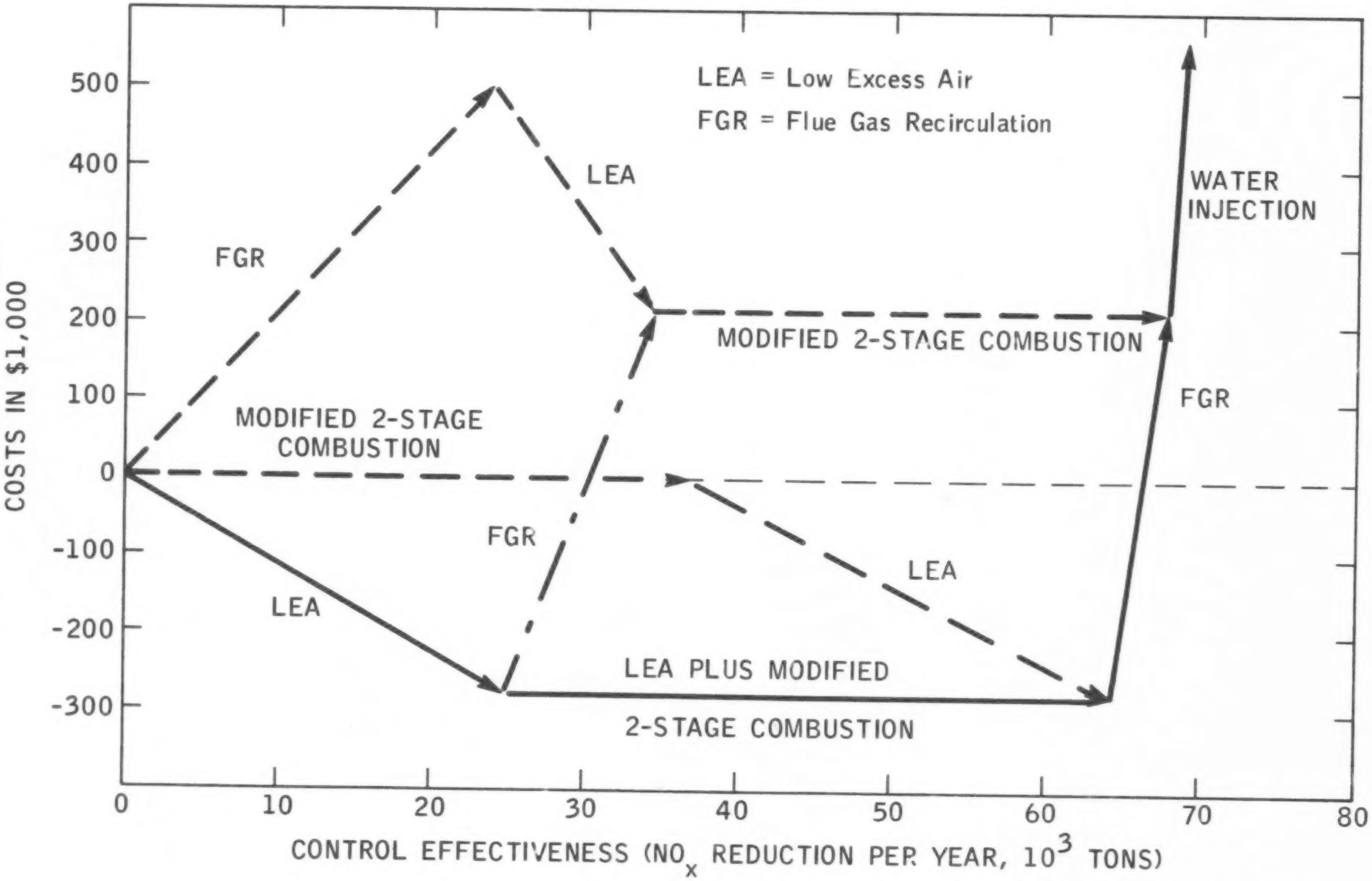

Table 9-7

Estimated Control Costs Per Ton NO_x Reduced - 750 MW Boiler

(Sensitivity to Emission Rates)

Control Method	Total Control Costs Per Year ($1000)		Gas Fired				Oil Fired			
			Measured Emission Factors		L.A. Emission Curves (9-1)		Measured Emission Factors		L.A. Emission Curves (9-1)	
	Gas	Oil	Tons NO_x Per Year	$/Ton	Tons NO_x Per Year	$/Ton	Tons NO_x Per Year	$/Ton	Tons NO_x Per Year	$/Ton
1. No Controls - Tons Emitted (0% NO_x Reduction)	0		38,528*	--	8,460*	--	9,773*	--	17,640*	--
2. Low Excess Air (33% NO_x Red. Gas or Oil)	(80)	(185)	12,714	(629)	2,792	(28.65)	3,225	(57.36)	5,821	(31.78)
3. Modified 2-Stage Comb. (50% Red. Gas; 40% on Oil)	0	0	19,264	0	4,230	0	3,909	0	7,056	0
4. Low Air + 2-Stage (90% Red. Gas; 73% Oil	(80)	(185)	34,675	(2.31)	7,614	(24.30)	7,134	(25.93)	12,877	(14.37)
5. Gas Recirculation (33% Red. Gas or Oil)	149	149	12,714	11.72	2,792	53.37	3,225	46.20	5,821	25.60
6. Water Injection (10% NO_x Red. Gas or Oil)	116	113	3,853	30.11	846	133.57	977	118.73	1,764	64.06

* Tons emitted per year.

Table 9-8

Estimated Control Costs per Ton NO_x Reduced - 120 MW Boiler

(Sensitivity to Emission Rates)

Control Method (% NO_x Reduction)	Total Control Costs Per Year ($1000)		Gas Fired				Oil Fired			
			Measured Emission Factor		L.A. Emission Curves (9-1)		Measured Emission Factors		L.A. Emission Factors (9-1)	
	Gas	Oil	Tons NO_x Reduced Per Year	Control Costs - $/Ton	Tons NO_x Reduced Per Year	Control Costs $/Ton	Tons NO_x Reduced Per Year	Control Costs - $/Ton	Tons NO_x Reduced Per Year	Control Costs - $/Ton
1. No Controls - Tons Emitted (% NO_x Reduction)	0		1,552*	--	1,032*	--	2,061*	--	2107*	--
2. Low Excess Air (33% on Gas: 30% on Oil)	(8.7)	(24.7)	512	(16.99)	341	(25.51)	618	(39.97)	621	(39.77)
3. Two-Stage Combustion (40% on Gas; 30% on Oil)	0	0	621	0	413	0	618	0	621	0
4. Low Air + 2-Stage (66% on Gas; 60% on Oil)	(8.7)	(24.7)	1,024	(8.50)	682	(12.76)	1,236	(19.98)	1,242	(19.89)
5. Gas Recirculation (25% on Gas; 30% on Oil)	32.2	32.2	388	82.99	258	124.81	618	52.10	621	51.85
6. Water Injection (10% on Gas or Oil)	18.3	18.3	155	118.06	103	177.66	206	88.83	211	86.73

* Tons emitted per year.

differences in the case of gas firing. From these examples, it appears that cost-effectiveness ratios are very sensitive to the emission rate assumptions used.

Alternate cost assumptions can lead to widely differing cost-effectiveness ratios for some control methods. For example, assuming that two-stage combustion hardware must be constructed instead of using "modified" two-stage combustion on the 750 MW gas fired boiler would result in total costs per year of $273,000* instead of a cost reduction of $80,000. Additional experience is needed in order to verify the lower costs actually obtained on the few boilers currently using this technique. Section 9.2 below illustrates the range of cost effectiveness profiles for two cost alternatives applied to Los Angeles County.

9.2 COST EFFECTIVENESS ANALYSIS FOR NO_x CONTROL VIA COMBUSTION MODIFICATIONS OF LOS ANGELES COUNTY GAS AND OIL-FIRED UTILITY BOILERS

Table 9-9 lists the number of steam boilers, electricity generating capacity and estimated annual NO_x emission for each generating plant currently operating in Los Angeles County. NO_x emissions were calculated from data supplied on the steam-electric questionnaire from two major utility companies. The emissions from the other plants located in Los Angeles County were estimated from fuel consumption data listed in Steam-Electric Plant Factors/1968 Edition of the National Coal Association (9-5), and Public Health Service Emission Factors (9-2) Complete emission data (controlled and uncontrolled) were applied where available. Similar ratios were applied to the plants where operating data were available. No controls were assumed for the other plants. These estimates are valid for 1980,assuming no additional steam electric plants will be constructed in Los Angeles County (9-4).

Cost-effectiveness data were calculated for each of the 60 boilers shown in Table 9-9 according to the methods described in detail above in Section 9.1. Figure 9-2 summarizes these data in the form of cost effectiveness profiles. The solid line-segments indicate the cost effectiveness path based on the following controls: substitution of "low sulfur oil" for cracked residual oil, present 2-stage combustion, low excess air, additional 2-stage combustion, gas recirculation and water injection . The low costs for the solid lines representing low excess air and modified two-stage combustion are based on the actual costs experience at the Moss Landing station of the Pacific Gas & Electric Company. The dashed line segments are based on the costs developed through consultation with Babcock and Wilcox company representatives as discussed in Section 8. The combination of "low sulfur oil" with its lower nitrogen content and some two-stage combustion represents

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* Based on $1,560,000 capital equipment costs from section 8, plus NAPCA Guidelines for other cost items.

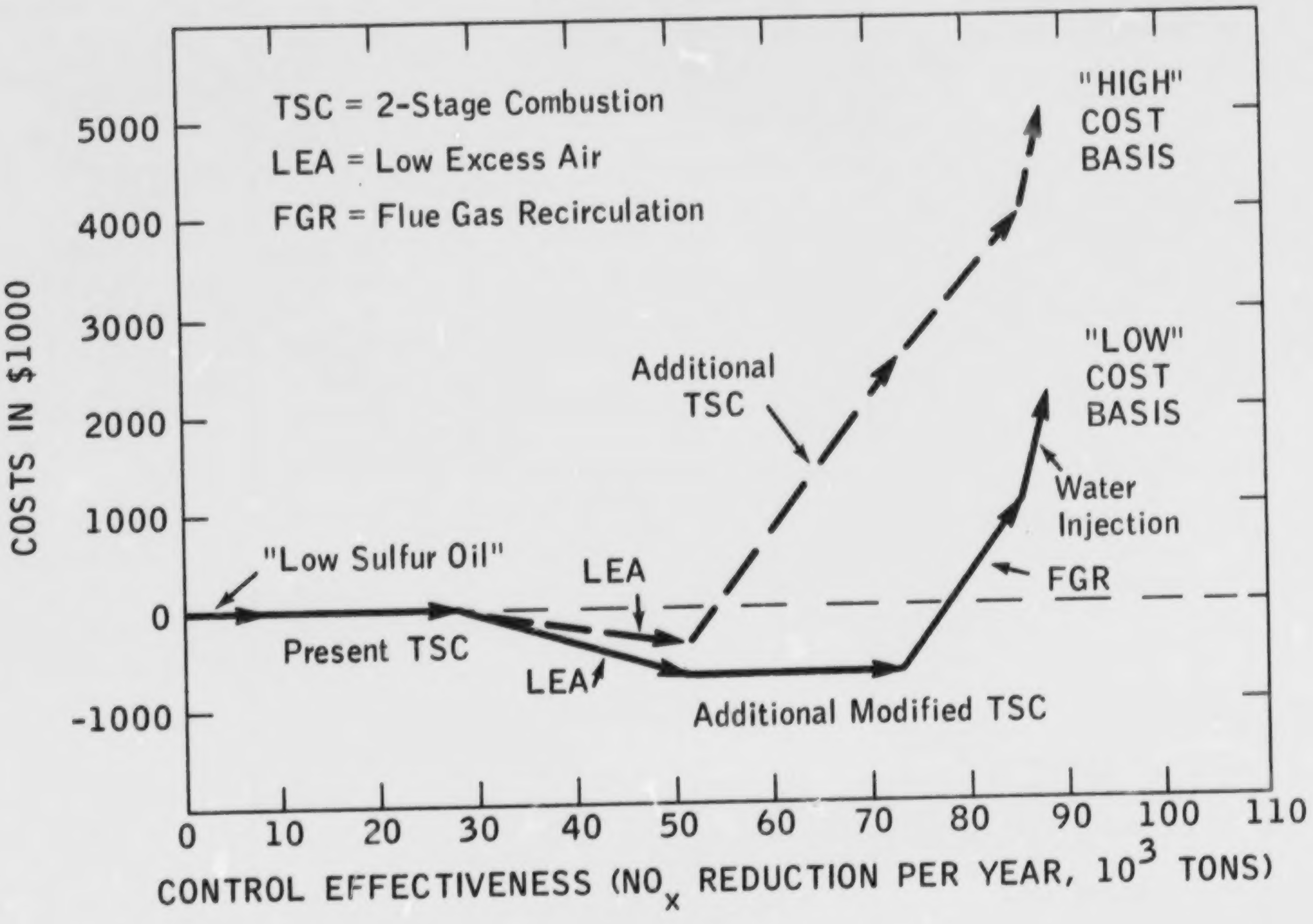
TABLE 9-9

LOS ANGELES COUNTY STEAM-ELECTRIC PLANTS

Utility Company and Plant	No. of Boilers (9-4)	Electric Capacity (Megawatts)	Est. NO_x Emissions - Tons/Yr	
			No Control	Present Control
So. Calif. Edison Co.				
Alamitos	6	1,950	32,531	21,990
El Segundo	4	1,020	10,851	8,838
Redondo Beach	11	1,530	28,390	16,848
Total	21	4,500	71,812	47,676
L.A. Dept. of W. & P.				
Harbor	5	355	4,544	4,085
Haynes	6	1,580	20,439	19,057
Scattergood	2	312	6,184	5,730
Valley	4	512	4,307	3,759
Total	17	2,759	35,474	32,631
City of Pasadena				
Broadway	3	158	1,130	1,130
Glenarm	6	72	1,076	1,076
Total	9	230	2,206	2,206
City of Burbank				
Magnolia	5	70	264	264
Olive	2	104	1,334	1,334
Total	7	174	1,598	1,598
City of Glendale	6	153	126	126
Grand Total	60	7,816	111,216	84,237

Figure 9-2

COST-EFFECTIVENESS PROFILES
LOS ANGELES COUNTY



existing controls already established. Since the costs involved in existing controls have already been expended for two-stage combustion, and the higher cost of "low sulfur" fuel was incurred to reduce sulfur oxide emissions, no incremental costs are shown for NO_x reduction. These cost-effectiveness profiles indicate a reasonable range, within which actual results based on experimentation will probably lie. We feel that potentially, the results of a R&D study conducted through designed experiments, plus optimization will lie closer to the solid line path than to the higher dashed path. For example, our assumed costs for flue gas recirculation are based upon the addition of a recirculatory fan with its high operating costs. However, there is a strong possibility that this additional fan can be eliminated by tying in the flue gas duct to the forced draft fan intake.

Since only gas and oil are burned in Los Angeles County boilers, NO_x reduction for existing boilers must be based on combustion modification. Flue gas scrubbing, even though it may be proven successful through research and development, is estimated to be much less economic than combustion modification for small to medium size gas and oil fired boilers. In section 9.3, the cost effectiveness of both combustion modifications and flue gas scrubbing methods will be evaluated for a predominantly coal burning region.

Control techniques implied in the above analysis are the use of nuclear and remotely located fossil fuel plants to supply increased electricity demand in the future. These factors will be considered explicitly in the Chicago area cost-effectiveness analysis in Section 9-3, below. With electric energy doubling every 9 years in Los Angeles County, demand is expected to increase to 100 billion kilowatt hours in 1980 (9-4) compared to about 39 billion KWH in 1968. Thus, if all of this electricity were generated within Los Angeles County at emission rates comparable to present, NO_x emission could increase to 215,000 tons of NO_x, compared to an estimated 84,000 tons of NO_x generated from power plants in 1968 as shown in Table 9-9.

9.3 COST-EFFECTIVENESS ANALYSIS OF NO_x CONTROL METHODS FOR CHICAGO REGION POWER PLANT BOILERS

Section 9.2 described NO_x combustion control cost effectiveness for gas and oil fired power boilers in Los Angeles County. This section will describe the cost effectiveness analysis for an area where power boilers are predominantly fired with coal. Thus, NO_x control using flue gas scrubbing will be considered along with combustion modification. The six county region of northeastern Illinois encompassing Chicago will be used to illustrate this analysis. Coal has been the predominant fuel burned in power stations in this region and historical data as well as control plans (9-5, 9-7) are available to serve as a basis for illustrative purposes.

Table 9-10 lists 9 power plants located within the six county Chicago region, with their estimated NO_x emission, fuel consumption, generating capacity, net generation and average stack height for the year 1965. Estimated 1980 net generation will amount to 104 billion kilowatt hours (9-7), a very large increase from the 36 billion kilowatt hours of net generation for 1967 (9-3).

If the estimated 1980 (9-7) demand for electricity were completely met by building new large fossil burning boilers, potential uncontrolled NO_x emission could increase to 508,000 tons as shown below in Table 9-11.

Table 9-11

Estimated 1980 Electric Generation

Plant	Capacity (MW)	Ave. Load Factor (%)	Net Generation (10^9 KWH)	NO_x Emissions (10^3 Tons)
1967	7600 (9-3)	54%	36 (9-3)	169
Mine Mouth	1800	75	12	60
Added Capacity	7890	80	56	279
Total	17,290	--	104	508

Table 9-10

Chicago Area Power Generating Plants (9-5)

Power Plant	Estimated NO_x Emissions (Tons)	Year 1965				Ave. Stack Height (Ft)
		Fuel Consumed		Net Generation 10^6 KWH	Capacity (MW)	
		Coal (10^3 Tons)	Gas (10^6 Cu Ft)			
				(9-6)	(9-6)	
1. Calumet (1)	2,258	198	2,007	438	246	300
2. Crawford (1)	20,820	1,748	2,469	3,956	702	375
3. Fisk (1)	10,007	964	2,666	2,157	602	400
4. Joliet (3)	26,630	2,663	--	5,594	1,202	500
5. Northwest (1)	1,580	158	--	193	224	310
6. Ridgeland (2)	17,844	1,765	1,410	3,491	690	213
7. Waukegan (3)	19,837	1,874	7,978	4,946	1,108	410
8. Will County (3)	31,580	3,158	--	6,688	1,269	440
9. State Line (2)	17,832	1,659	9,038	4.738	972	400
Total	148,388	14,187				

1. Located within Chicago.
2. Located near City boundries.
3. Located more than 15 miles from City.

Table 9-12 contains data on a possible boiler population for the year 1980, based on the assumptions listed above. Gas fired boilers are assumed to generate over 30% (11.3 out of 36.3 billion KWH) of fossil fuel demand, vs. about 10% in 1967, due to substitution of gas for 4.4 million tons of coal burned in Chicago stations by 1980. Estimated NO_x emissions and load factors are consistent with the assumed composite boilers described in Section 9-4.

Table 9-13 contains a summary of cost and effectiveness data for the boilers shown in Table 9-12. The development of control costs and effectiveness of these boilers will be described in Section 9-4. The cost per ton of NO_x reduced varies from a low of $-11 (saving) for low excess air on three 750 MW coal fired boilers, to a high of $68 (cost) for low excess air plus flue gas recirculation on a 500 MW gas fired boiler. The circled numbers within the Table indicate the boiler-control combinations that should be used in establishing the lowest control cost for a given NO_x control objective. It should be noted that two-stage combustion and flue gas recirculation controls would not be applied singly, since other boiler control combinations will result in higher NO_x reduction at equal or reduced cost.

Now we are in a position to develop cost effectiveness profiles considering both combustion and flue gas controls as shown in Figure 9-3. The solid line indicates the minimum cost path when applying combustion control only. The dashed line indicates the minimum cost path for applying boiler controls for an ultimate NO_x reduction target of 114 thousand tons of NO_x. In addition, terminal points are shown for other possible paths (not shown). These points would not normally be considered as practical since in general, the paths to these points are higher than other paths shown, thus a decision to reduce NO_x emissions further would generally result in higher costs. Table 9-14 illustrates the calculation of the cost-effectiveness paths plotted on Figure 9-3, while Table 9-15 summarizes the calculation of the plotted terminal points.

Summarizing this section, it is important to note that the Chicago region would produce an estimated total of 508,000 tons of NO_x from power boilers (Table 9-11) in 1980 on an uncontrolled basis, compared to actual NO_x emissions of about 148,000 tons in 1965. Using our assumptions, it is seen that use of nuclear generation reduces potential NO_x emissions by 279 thousand tons while remote minemouth generation results in a further reduction of 60,000 tons.* The remaining 169 thousand tons (Table 9-12) can be reduced through combustion and flue gas scrubbing control to a minimum level of 55,000 tons (37% of the 1965 NO_x emission level) at an estimated annual cost of $2 million. However, a reduction to 66% of 1965 levels, 98,000 tons, might be obtained at an estimated cost of only $245,000 per year by proceding through step 7 of the combustion control path.

* It is likely that, long range, minemouth location will not provide adequate control, and therefore control engineering steps will be needed for all fossil fuel burning power plants.

Table 9-12

Assumed Chicago Area Fossil Fuel Boilers

Boiler Capacity	NO_x Emissions/Boiler			No. of Boilers	Net Generation (10^9 KWH)	NO_x Emiss. (10^3 Tons)
	ppm	lb/hr	Tons/Year			
Coal Fired Boilers:						
250 MW	573	1,237	4,884	10	8.7	49
500 MW	610	4,847	12,748	1	2.6	13
750 MW	665	7,325	22,414	3	13.7	67
Gas Fired Boilers:						
250 MW	328	2,478	2,438	10	8.7	24
500 MW	851	5,900	15,517	1	2.6	16
Total				25	36.3	169

Table 9-13

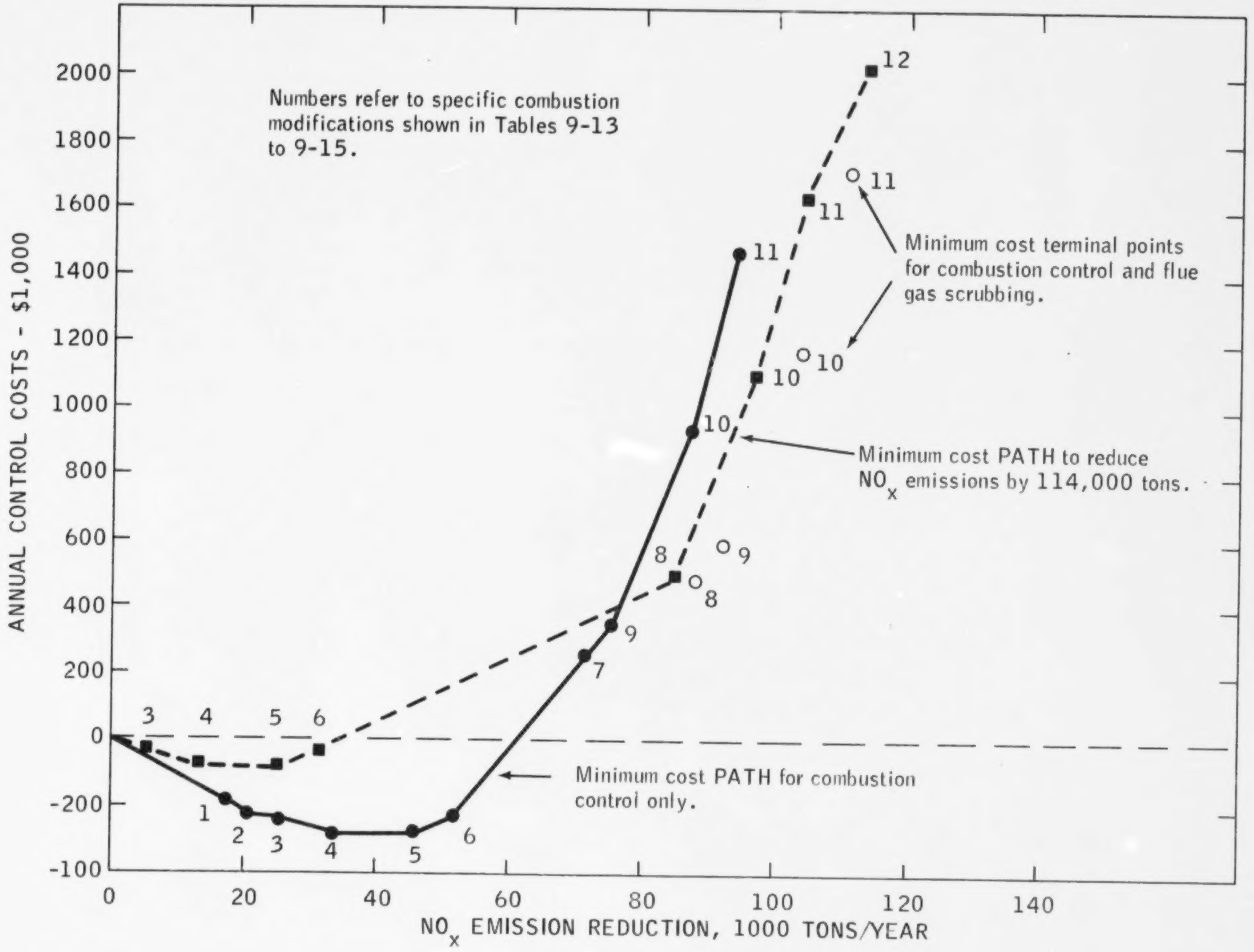
Cost Effectiveness Summary - 1980 Chicago Area Fossil Fuel Boilers

Control Method		Boilers				
		Coal Fired			Gas Fired	
		3 @ 750 MW	1 @ 500 MW	10 @ 250 MW	1 @ 500 MW	10 @ 250 MW
1. Low Excess Air (LEA)	Cost, \$ NO_x-Tons \$/Ton	-177,000 ①* 16,800 -11	-27,000 ② 3,200 -9	0 ⑤ 12,000 0	-35,000 ③ 5,100 -7	-40,000 ④ 8,000 -5
2. 2-Stage Combustion	Cost, \$ NO_x-Tons \$/Ton	720,000 23,400 31	176,000 4,500 39	1,030,000 15,000 69	44,000 7,800 56	520,000 11,000 47
3. LEA Plus 2-Stage Combustion	Cost, \$ NO_x-Tons \$/Ton	543,000 40,200 13	148,000 7,000 23	1,040,000 24,000 43	9,000 ⑥ 10,900 0.8	490,000 ⑪ 15,000 33
4. Flue Gas Recirculation (FGR)	Cost, \$ NO_x-Tons \$/Ton	480,000 22,200 22	109,000 4,200 26	580,000 15,000 39	109,000 5,100 21	510,000 7,000 83
5. LEA Plus FGR	Cost, \$ NO_x-Tons \$/Ton	303,000 ⑦ 36,900 8.2	82,000 ⑨ 7,000 12	590,000 ⑩ 24,000 24	740,000 10,900 68	550,000 15,000 37
6 $Mg(OH)_2$ Flue Gas Scrubbing	Cost, \$ NO_x-Tons \$/Ton	538,000 ⑧ 53,000 10	408,000 ⑫ 10,198 40	--	--	--

* Circled numbers are priority indicators.

Figure 9-3

COST EFFECTIVENESS PROFILES FOR NO_x CONTROL - CHICAGO AREA



Numbers refer to specific combustion modifications shown in Tables 9-13 to 9-15.

Minimum cost terminal points for combustion control and flue gas scrubbing.

Minimum cost PATH to reduce NO_x emissions by 114,000 tons.

Minimum cost PATH for combustion control only.

Table 9-14

Minimum Cost NO_x Control Paths for Chicago Region Power Plants

Path I - Combustion Modification Only

Boiler Size (MW)	Fuel Burned	Control Method	Cost ($/Ton)	NO_x Removed/Yr (10^3 Tons)		Cost/Year ($1000)	
				Indi-vidual	Cumulative	Indi-vidual	Cumulative
1. 750	Coal	LEA*	-11	17	17	-177	-177
2. 500	Coal	LEA	- 9	3	20	- 27	-204
3. 500	Gas	LEA	- 7	5	25	- 35	-239
4. 250	Gas	LEA	- 5	8	33	- 40	-279
5. 250	Coal	LEA	0	12	45	0	-279
6. 500	Gas	LEA + 2 St.C.**	1	11	51	9	-235
7. 750	Coal	LEA + FGR***	8	37	71	303	245
9. 500	Coal	LEA + FGR	12	7	75	82	354
10. 250	Coal	LEA + FGR	24	24	87	590	944
11. 250	Gas	LEA + 2 St.C.	33	15	94	490	1474

Path II - Flue Gas Scrubbing And Combustion Modification to Reach 114,000 Ton Reduction

3. 500	Gas	LEA	- 7	5	5	- 35	- 35
4. 250	Gas	LEA	- 5	8	13	- 40	- 75
5. 250	Coal	LEA	0	12	25	0	- 75
6. 500	Gas	LEA + 2 St.C.	1	11	31	9	- 31
8. 750	Coal	$Mg(OH)_2$	10	54	85	538	507
10. 250	Coal	LEA + FGR	24	24	97	590	1097
11. 250	Gas	LEA + 2 St.C.	33	15	104	490	1627
12. 500	Coal	$Mg(OH)_2$	40	10	114	408	2036

* LEA = Low Excess Air
** 2 St.C.= Two Stage Combustion
*** FGR = Flue Gas Recirculation

Table 9-15

Optimum Cost-Effectiveness Profile for NO_x Control
Chicago Region - 1980 Target

Boiler Size (MW)	Fuel Burned	Control Method	Cost ($/Ton)	NO_x Removed/Yr (10^3 Tons)		Costs/Year ($1000)	
				Indi-vidual	Cumulative	Indi-vidual	Cumulative
No Control (Base Case)					(508)		(0)
Present Plans:							
1. 500-1000		Nuclear	0 (1)	279	279	0	0
2. 600	Coal	Remote Minemouth	0 (1)	60	339	0	0
Boiler Controls:							
1. 750	Coal	LEA	-11	17	17	-177	-177
2. 500	Coal	LEA	- 9	3	20	- 27	-204
3. 500	Gas	LEA	- 7	5	25	- 35	-239
4. 250	Gas	LEA	- 5	8	33	- 40	-279
5. 250	Coal	LEA	0	12	45	0	-279
6. 500	Gas	LEA + 2 St.C.	1	11	51	9	-235
7. 750	Coal	LEA + FGR	8	37	71	303	245
8. 750	Coal	$Mg(OH)_2$	10	54	88	538	480
9. 500	Coal	LEA + FGR	12	7	92	82	589
10. 250	Coal	LEA + FGR	24	24	104	590	1179
11. 250	Gas	LEA + 2 St.C.	33	15	111	490	1709
12. 500	Coal	$Mg(OH)_2$	40	10	114	408	2035

(1) Nuclear and minemouth plants are assumed to be economically competitive with large fossil fuel plants.

However, plans (9-5, 9-7) have been made to control air pollution in this region. These control plans include substantial expansion of nuclear generation, remote minemouth coal plants, substitution of gas for some coal burned within Chicago, and no new coal plants in or close to Chicago. To illustrate cost effectiveness analyses applied to this region we will make the following simplifying assumptions for the year 1980:

1) 7890 megawatts of nuclear capacity operating at 80% load factor will generate 56 billion KWH of electricity.*
2) Three 600 MW minemouth boilers will operate at 75% load factor generating 12 billion KWH of electricity.*
3) 1967 capacity (7600 megawatts) will be generated by modern fossil fuel boilers.**

On the basis of these assumptions NO_x combustion and flue gas controls would be applied only to the 35% of total generation represented by 1967 capacity, since nuclear generation produces no NO_x emissions and the minemouth plants are assumed far enough from population centers to require no NO_x controls.***

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* Plans have been announced for the construction of a significant portion of this capacity by 1974.

** Fossil fuel capacity would be lowered if planned nuclear expansion can be accomplished. However recent slow-downs in delivery of nuclear generating equipment raise doubts in accomplishing planned expansion schedules.

*** As discussed above, minemouth location is likely to be an "interim" control method.

9.4 COST EFFECTIVENESS FOR NO_x CONTROL OF POWER BOILERS

In this section, the basic assumptions and detailed calculations underlying cost effectiveness analyses for NO_x control of power boilers will be discussed. The resulting data from this section will then serve as input to develop the Cost-Effectiveness Profiles of Section 9.5, Power Generation in the United States and Section 9.6, Major Combustion Sources in the U.S.

Almost all power boilers operating in the United States are custom-made to customer specifications. Specifications are based upon a complex set of interacting construction and operating cost variables such as unit capacity, fuel type and quality, type of firing, etc. Thus to reduce the variety of boilers to a manageable size for analysis, it was decided to represent all of the fossil fuel burning boilers by 15 "composite" boilers: gas, oil and coal fired boilers supplying steam for turbogenerators of 1000, 750, 500, 250 and 120 megawatt capacity. Since two boilers of the same size, burning identical fuels have different average NO_x emission rates due to different design features such as type of firing, none of the 15 "composite" boilers represent any actual single boiler, but are assumed to represent the average of all United States boilers in its size--fuel class operating in the year 1980.

Sections 4, 5 and 8 have discussed the % effectiveness and control costs for combustion and flue gas control applicable to various steam boilers. Table 9-16 summarizes our estimates of uncontrolled NO_x emissions. These estimated average emission factors are plotted in Figure 9-4 in comparison with the Los Angeles Joint Project (9-1) emission curves for oil and gas. Since only boilers of less than 200 megawatt capacity were included in the Joint Project, most of our estimated emissions must be compared with extrapolations of the curves. The estimated emission factors for oil and coal lie close to a simple extrapolation of the Joint Study "Oil" curve. However, the estimated composite boiler gas fired emissions have a slope considerably greater than the extrapolated Joint Study "Gas" curve.* These NO_x estimates were developed by weighting measured emission rates according to the expected proportions of tangentially fired boilers to horizontally opposed fired boilers. The composite 120 megawatt size boilers are expected to have emissions equal to those estimated for the Los Angeles Joint Study curves.

Tables 9-17 through 9-21 contain estimated control costs per ton of NO_x reduced, for individual composite boilers of 1000 megawatts to 120 megawatt capacity. The % NO_x reduction data are taken from Table 4-5, Section 4, while control cost data are taken from Section 8. From Table 9-17, it is seen that control costs per ton of NO_x removed vary from a low of -$30 per ton (profit or reduction in operating costs) to a high of $60 per ton. In Section 9.5, these tables will be used with estimates of number of boilers in each of the 15 fuel-size groups to establish cost effectiveness profiles for all U.S. power boilers.

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* See previous discussion in Section 3.3.

Table 9-16

Esso Systems Study Estimated NO_x Emissions From Composite Boilers

Boiler Size and Fuel	NO_x Emissions			% Load Factor Hours Per Yr.	Heat Rate BTU's Per KWH
	Parts Per Million	Lbs NO_x Per Hour	Tons NO_x Per Year		
1000 MW				(70%)	
Gas	1,400	17,320	53,000	6,120	8,390
Oil	700	9,803	30,000	6,120	8,100
Coal	700	9,803	30,000	6,120	8,100
750 MW				(70%)	
Gas	987	9,516	29,120	6,120	8,720
Oil	665	7,325	22,414	6,120	8,500
Coal	665	7,325	22,414	6,120	8,500
500 MW				(60%)	
Gas	851	5,900	15,517	5,260	9,400
Oil	610	4,847	12,748	5,260	9,200
Coal	610	4,847	12,748	5,260	9,200
250 MW				(45%)	
Gas	328	1,237	2,438	3,942	10,200
Oil	573	2,478	4,884	3,942	10,000
Coal	573	2,478	4,884	3,942	10,000
120 MW				(25%)	
Gas	237	457	500	2,190	10,920
Oil	511	1,131	1,238	2,190	10,670
Coal	511	1,131	1,238	2,190	10,670

Figure 9-4

ESTIMATED NO_x EMISSION RATES - COMPOSITE BOILERS

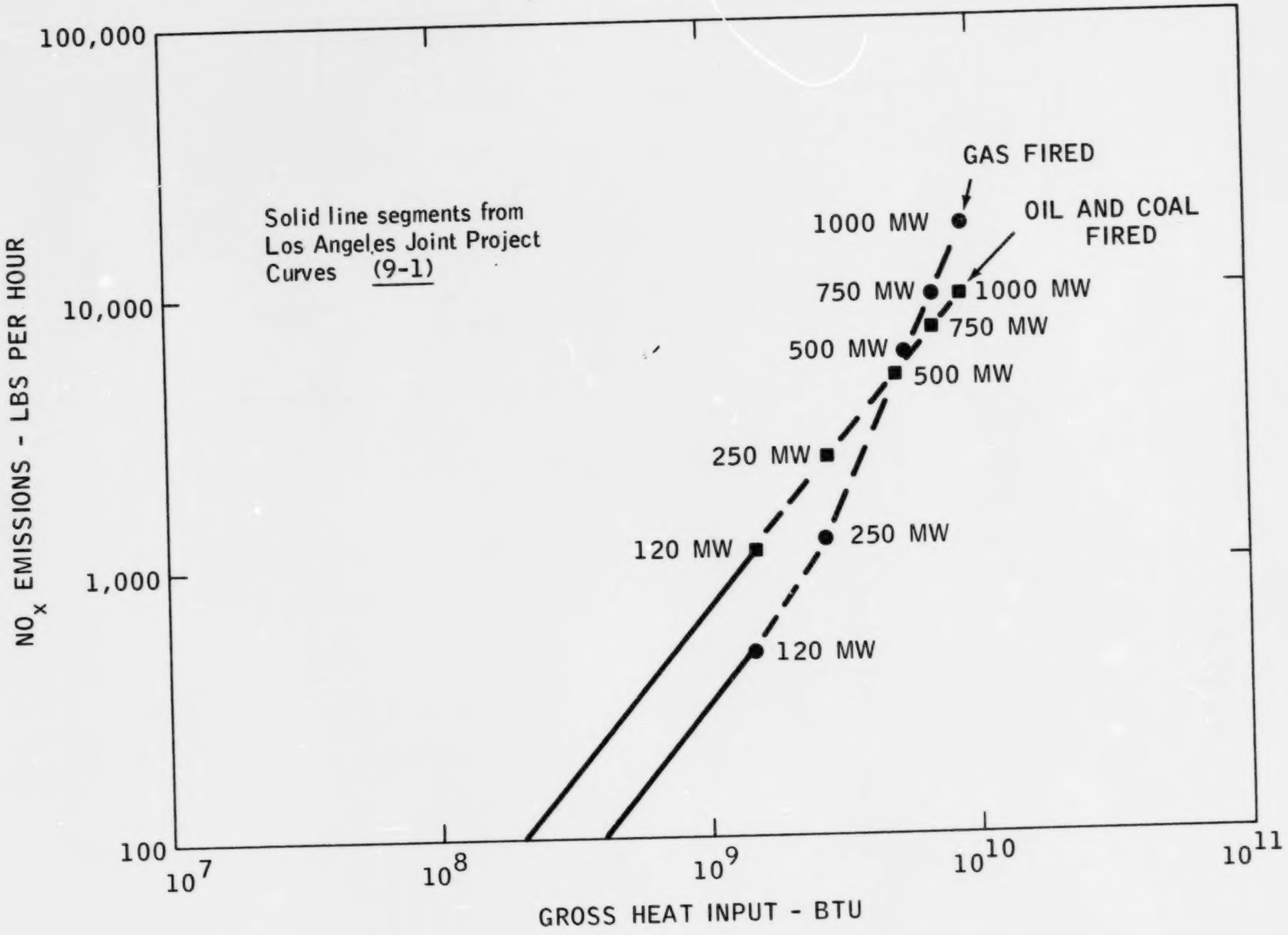

Table 9-17

Estimated Control Costs Per Ton of NO_x Reduced: 1000 MW Boiler at 6120 Hours/Year

Control Method	% NO_x Reduction*	Fuel Used	Cost Per Year \$1,000**	NO_x Reduction 1000's of Tons/Yr.	Control Costs		
					\$/Ton NO_x	Mils/KWH	\$/Ton Coal Fired
Uncontrolled (Base Case)	0	Gas	0	53.0***	0	0	--
	0	Oil	0	30.0***	0	0	--
	0	Coal	0	30.0***	0	0	0
1. Low Excess Air	33	Gas	-95	17.5	-5	-0.02	--
	33	Oil	-297	9.9	-30	-0.05	--
	25	Coal	-79	7.5	-11	-0.01	-0.04
2. Two-Stage Combustion	50	Gas	0	26.5	0	0	--
	40	Oil	0	12.0	0	0	--
	35	Coal	299	10.5	29	0.05	0.14
3. Low Excess Air Plus 2-Stage Combustion	90	Gas	-95	47.7	-2	-0.02	--
	73	Oil	-297	21.9	-14	-0.05	--
	60	Coal	220	18.0	12	0.04	0.10
4. Flue Gas Recirculation	33	Gas	202	17.5	12	0.03	--
	33	Oil	202	9.9	20	0.03	--
	33	Coal	202	9.9	20	0.03	0.09
5. Low Excess Air Plus Flue Gas Recirculation	80	Gas	107	42.4	3	0.02	--
	70	Oil	-95	21.0	-5	-0.02	--
	55	Coal	123	16.5	8	0.02	0.06
6. Water Injection	10	Gas	144	5.3	27	0.02	--
	10	Oil	179	3.0	60	0.03	--
	10	Coal	143	3.0	48	0.02	0.07
7. Flue Gas Scrubbing $Mg(OH)_2$		Gas	--	--	--	--	--
	80	Oil	510	24	21	0.08	--
	80	Coal	-122	24	-5	-0.02	0.06

* From Section 4. (Table 4-5).

** From Section 8.

*** 1000's of tons of NO_x emitted from an uncontrolled boiler.

Table 9-18

Estimated Control Costs Per Ton of NO_x Reduced: 750 MW Boiler at 6120 Hours/Year

Control Method	% NO_x Reduction*	Fuel Used	Cost Per Year $1,000**	NO_x Reduction 1000's of Tons/Yr.	Control Costs		
					$/Ton NO_x	$\frac{\text{Mils}}{\text{KWH}}$	$/Ton Coal Fired
Uncontrolled (Base Case)	0 0 0	Gas Oil Coal	0 0 0	29.1*** 22.4*** 22.4***	0 0 0	0 0 0	-- -- 0
1. Low Excess Air	33 33 25	Gas Oil Coal	-68 -226 -59	9.6 7.4 5.6	-7 -31 -11	-0.01 -0.05 -0.01	-- -- -0.04
2. Two-Stage Combustion	50 40 35	Gas Oil Coal	24 24 240	14.6 9.0 7.8	2 3 31	0.01 0.01 0.05	-- -- 0.14
3. Low Excess Air Plus 2-Stage Comb.	85 73 60	Gas Oil Coal	-45 -203 181	24.8 16.4 13.4	-2 -12 14	-0.01 -0.04 0.04	-- -- 0.11
4. Flue Gas Recirculation	33 33 33	Gas Oil Coal	160 160 160	9.6 7.4 7.4	17 22 22	0.03 0.03 0.03	-- -- 0.10
5. Low Excess Air Plus Flue Gas Recirc.	80 70 55	Gas Oil Coal	91 -67 101	23.2 15.7 12.3	4 -4 8	0.02 -0.01 0.02	-- -- 0.06
6. Water Injection	10 10 10	Gas Oil Coal	114 141 113	2.9 2.2 2.2	39 64 51	0.02 0.03 0.02	-- -- 0.07
7. Flue Gas Scrubbing $Mg(OH)_2$	80	Gas Oil Coal	-- -- 179****	-- -- 17.9****	-- -- 10****	-- -- 0.04****	-- -- 0.11****

* From Section 4. (Table 4-5)

** From Section 8.

*** 1000's of tons of NO_x emitted from an uncontrolled boiler.

**** By interpolation of 1000 MW and 500 MW plant data.

Table 9-19

Estimated Control Costs Per Ton of NO_x: Reduced 500 MW Boiler at 5620 Hours/Year

Control Method	% NO_x Reduction	Fuel Used	Cost Per Year $1,000**	NO_x Reduction 1000's of Tons/Yr.	Control Costs		
					$/Ton NO_x	Mils KWH	$/Ton Coal Fired
Uncontrolled (Base Case)	0	Gas	0	15.52***	0	0	--
	0	Oil	0	12.75***	0	0	--
	0	Coal	0	12.75***	0	0	0
1. Low Excess Air	33	Gas	-35	5.1	-7	-0.01	--
	33	Oil	-132	4.2	-32	-0.05	--
	25	Coal	-27	3.2	-8	-0.01	-0.03
2. Two-Stage Combustion	50	Gas	44	7.8	6	0.02	--
	40	Oil	44	5.1	9	0.02	--
	35	Coal	176	4.5	39	0.06	0.17
3. Low Excess Air Plus 2-Stage Combustion	70	Gas	9	10.9	1	0.01	--
	65	Oil	-88	8.3	11	-0.03	--
	55	Coal	148	7.0	21	0.05	0.14
4. Flue Gas Recirculation	33	Gas	109	5.1	21	0.04	--
	33	Oil	109	4.2	26	0.04	--
	33	Coal	109	4.2	26	0.04	0.10
5. Low Excess Air Plus Flue Gas Recirculation	70	Gas	74	10.9	7	0.03	--
	65	Oil	-23	8.3	-3	-0.01	--
	55	Coal	82	7.0	12	0.03	0.08
6. Water Injection	10	Gas	71	1.6	44	0.03	--
	10	Oil	87	1.3	67	0.03	--
	10	Coal	70	1.3	54	0.03	0.07
7. Flue Gas Scrubbing-$Mg(OH)_2$		Gas					--
		Oil					--
	80	Coal	398	10.2	39	0.15	0.38

* From Section 4. (Table 4-5)

** From Section 8.

*** 1000's of tons of NO_x emitted from an uncontrolled boiler.

Table 9-20

Estimated Control Costs Per Ton of NO_x: Reduced 250 MW Boiler at 3942 Hours/Year

Control Method	% NO_x Reduction	Fuel Used	Cost Per Year $1,000**	NO_x Reduction 1000's of Tons/Yr.	Control Costs		
					$ Ton NO_x	Mils KWH	$/Ton Coal Fired
Uncontrolled (Base Case)	0	Gas	0	2.44***	0	0	--
	0	Oil	0	4.88***	0	0	--
	0	Coal	0	4.88***	0	0	0
1. Low Excess Air	33	Gas	-4	0.81	-5	<0.01	--
	30	Oil	-44	1.5	-29	-0.04	--
	25	Coal	0	1.2	0	0	0
2. Two Stage Combustion	45	Gas	52	1.1	47	0.05	--
	35	Oil	52	2.2	24	0.05	--
	30	Coal	103	1.5	69	0.10	0.24
3. Low Excess Air Plus 2-Stage Comb.	60	Gas	49	1.5	33	0.05	--
	55	Oil	9	2.9	3	0.01	--
	50	Coal	104	2.4	43	0.11	0.25
4. Flue Gas Recirculation	30	Gas	58	0.73	80	0.06	--
	30	Oil	58	1.5	39	0.06	--
	30	Coal	58	1.5	39	0.06	0.14
5. Low Excess Air Plus Flue Gas Recirc.	60	Gas	55	1.5	37	0.06	--
	55	Oil	15	2.7	6	0.02	--
	50	Coal	59	2.4	24	0.06	0.14
6. Water Injection	10	Gas	29	0.24	121	0.03	--
	10	Oil	36	0.49	74	0.04	--
	10	Coal	29	0.49	59	0.03	0.07
7. Flue Gas Scrubbing $Mg(OH)_2$		Gas	--	--	--	--	--
		Oil					
		Coal					

* From Section 4. (Table 4-5).

** From Section 8.

*** 1000's of tons of NO_x emitted from an uncontrolled boiler.

Table 9-21

Estimated Control Costs Per Ton of NO_x: Reduced 120 MW Boiler at 2190 Hours/Year

Control Method	% NO_x Reduction*	Fuel Used	Cost Per Year $1,000**	NO_x Reduction 1000's of Tons/Yr.	Control Costs		
					$/Ton NO_x	Mils KWH	$/Ton Coal Fired
Uncontrolled (Base Case)	0	Gas	0	.50***	0	0	--
	0	Oil	0	1.24***	0	0	--
	0	Coal	0	1.24***	0	0	0
1. Low Excess Air	33	Gas	10	0.17	60	0.04	--
	30	Oil	-2	0.37	-5	-0.01	--
	25	Coal	11	0.31	36	0.04	0.09
2. Two-Stage Combustion	40	Gas	54	.20	270	0.21	
	30	Oil	54	.37	146	0.21	--
	25	Coal	60	.31	194	0.23	0.50
3. Low Excess Air Plus 2-Stage Comb.	53	Gas	64	.27	237	0.24	--
	45	Oil	52	.56	93	0.20	--
	40	Coal	72	.50	144	0.27	0.60
4. Flue Gas Recirculation	30	Gas	24	.15	160	0.09	--
	30	Oil	30	.37	81	0.11	--
	30	Coal	30	.37	81	0.11	0.25
5. Low Excess Air Plus Flue Gas Recirc.	53	Gas	40	.27	148	0.15	--
	45	Oil	28	.56	50	0.11	--
	40	Coal	41	.50	83	0.16	0.34
6. Water Injection	10	Gas	9	.05	180	0.03	--
	10	Oil	11	.12	92	0.04	--
	10	Coal	9	.12	75	0.03	0.08
7. Flue Gas Scrubbing $Mg(OH)_2$		Gas	--	--	--	--	--
		Oil					
		Coal	528	1.0	530	2.01	4.40

* From Section 4. (Table 4-5)

** From Section 8.

*** 1000's of tons of NO_x emitted from an uncontrolled boiler.

9.5 COST-EFFECTIVENESS PROFILES OF NO_x CONTROL FOR POWER GENERATION IN THE UNITED STATES

In this section cost-effectiveness profiles are calculated for NO_x control of all fossil fuel power generation in the United States for the year 1980. Since section 9.4 established the cost per ton of NO_x removed for each control method, for each of the 15 "fuel-size" composite boilers, it will now be necessary to estimate the number of each of these boilers operating in 1980 so that estimated total costs effectiveness profiles can be developed.

The major steps used in developing the estimated population of fossil fuel boilers for 1980 were:

(1) Develop forecast for 1980 total U.S. electric generation.
(2) Estimate nuclear and hydro-generation in 1980.
(3) Estimate % of generation for each fossil fuel type
(4) Estimate the number of boilers required of each size (by fuel) to supply required net generation, considering average heat rates and load factors.

Table 9-22 below summarizes our Forecast of Electric Utility Generation for the year 1980, compared to selected private and published forecasts.

Table 9-22

Forecasts of 1980 Electric Utility Generation

Fuel	Quantity	BTUs Per Unit	Total BTU (10^{12})	Ave. Heat Rate (BTU/KWH)	U.S. Net Generation (10^9 KWH)
Gas	3.30×10^{12} Ft^3	1046	3,452	9280	372
Oil	250×10^6 Bbl	6.3×10^6	1,575	9490	166
Coal	445×10^6 Tons	23.8×10^6	10,591	8596	1232
Hydro					320
Nuclear					720
ER&E STUDY FORECAST - U.S. NET ELECTRIC GENERATION					2810
OTHER SELECTED FORECASTS:					
Federal Power Commission (9/69) (9-8)					3086
Edison Electric Institute (6/69) (9-9)					2895
Gibbs and Hill (9/69) (9-11)					2787
Private Service (8/69)					2594
Private Communication (3/69)					2730
Bureau of Mines (7/68) (9-12)					2739
Ebasco Services Inc. (4/68) (9-14)					2740
Average of Selected Forecasts					2796

Our forecast of 320 billion KWH from 1980 hydro generation is about equal to the average of available forecasts. Forecasts of nuclear generation vary over the very wide range of 631* to 1291 (9-11) billion KWH in the year 1980. Our estimate lies towards the lower end of the range and is derived from an estimated capacity of 110,000 megawatts operating at an 80% load factor.

Table 9-23 below summarizes the number and sizes of boilers by fuel assumed as a basis for cost effectiveness calculations.

Table 9-23

Fossil Fuel Boilers - 1980

Capacity Range (MW)	Average Net Generating Capacity	Number of Boilers by Fuel			
		Gas	Oil	Coal	Total
Less than 200	120	155	71	474	700
200-400	250	40	18	122	180
400-600	500	27	12	81	120
600-800	750	23	11	71	105
800 and over	1000	20	9	61	90
	Totals	265	121	809	1195

These estimates reflect current and past trends toward larger unit capacity as well as our estimates of interfuel competition and economics. For example, a recent TVA paper (9-15) estimated that over 95% of generating capacity to be installed after 1970 will be in units equal to, or greater than 600 megawatt capacity, and that by 1980 about one-half of all installed capacity will be in units of 600 megawatt capacity or larger.

Table 9-24 provides estimated control costs per ton of NO_x reduced for all United States 1000 MW boilers, using four potential control methods. Costs and control effectiveness for single boilers are taken from Table 9-17 and multiplied by the number of boilers (20 gas fired, 9 oil fired, and 61 coal fired) from Table 9-23 to obtain total costs and effectiveness. Two-stage combustion, water injection, and flue gas recirculation applied singly are not shown since other boiler control combinations result in higher NO_x reduction at equal or reduced costs. Tables 9-25 through 9-28 were constructed in the same manner as Table 9-24 for 750, 500, 250 and 120 megawatt power plant boilers, respectively.

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* Private Forecast.

Table 9-24

Estimated Control Costs per Ton of NO$_x$ Reduced
Total United States 1000 MW Boilers - 6120 Hours/year

Control Method	% NO$_x$ Reduction*	Fuel Used	Cost Per Year $1000**	NO$_x$ Reduction 1000's of Tons/Yr.	Control Costs $/Ton
Uncontrolled (Base Case)	0	Gas	0	1060***	0
	0	Oil	0	270***	0
	0	Coal	0	1830***	0
1. Low Exess Air	33	Gas	-1,900	350	-5
	33	Oil	-2,673	89	-30.0
	25	Coal	-4,819	458	-11 ⑤****
2. Low Excess Air Plus Two-Stage Combustion	90	Gas	-1,900	954	-2.0 ⑫
	73	Oil	-2,673	197	-14 ④
	60	Coal	13,420	1098	12 ㉔
3. Low Excess Air Plus Flue Gas Recirculation	80	Gas	2,140	848	3
	70	Oil	-855	189	-5
	55	Coal	7,503	1007	8 ⑱
4. Flue Gas Scrubbing - Mg(OH)$_2$	--	Gas	--	--	--
	80	Oil	4,590	216	21
	80	Coal	-7,437	1464	-5 Ⓐ

* From Section 4. (Table 4-5)

** From Section 8. (Tables 8-7, 8-8, 8-9 and 8-18).

*** 1000's of tons of NO$_x$ emitted from Uncontrolled Boilers.

**** Circled symbols are priority indicators.

Table 9-25

Estimated Control Costs per Ton of NO_x Reduced
Total United States 750 MW Boilers - 6120 Hours/Year

Control Method	% NO_x Reduction*	Fuel Used	Cost Per Year $1000**	NO_x Reduction 1000's of Tons/Yr.	Control Costs $/Ton
Uncontrolled (Base Case)	0	Gas	0	670***	0
	0	Oil	0	247***	0
	0	Coal	0	1591***	0
1. Low Excess Air	33	Gas	-1,564	221	-7 ⑧****
	33	Oil	-2,486	81	-31 ①
	25	Coal	-4,189	398	-11 ⑥
2. Low Excess Air Plus Two-Stage Combustion	85	Gas	-1,035	569	-2 ⑭
	73	Oil	-2,233	180	-12 ⑮
	60	Coal	12,851	955	14 ⑲
3. Low Excess Air Plus Flue Gas Recirculation	80	Gas	2,093	536	4
	70	Oil	-737	173	-4
	55	Coal	7,171	875	8 ⑱
4. Flue Gas Scrubbing - $Mg(OH)_2$	--	Gas	--	--	--
	--	Oil	--	--	--
	80	Coal	12,720	1273	10 Ⓑ

* From Section 4. (Table 4-5)

** From Section 8. (Appendix Tables)

*** 1000's of tons of NO_x emitted from Uncontrolled Boilers.

**** Circled symbols are priority indicators.

Table 9-26

Estimated Control Costs per Ton of NO_x Reduced Total United States 500 MW Boilers - 5620 Hours/Year

Control Method	% NO_x Reduction*	Fuel Used	Cost Per Year \$1000**	NO_x Reduction 1000's of Tons/Yr.	Control Costs \$/Ton
Uncontrolled (Base Case)	0	Gas	0	419***	0
	0	Oil	0	153***	0
	0	Coal	0	1033***	0
1. Low Excess Air	33	Gas	-945	138	-7 ⑨****
	33	Oil	-1,584	51	-31 ②
	25	Coal	-2,187	258	-9 ⑦
2. Low Excess Air Plus Two-Stage Combustion	70	Gas	243	293	1 ⑯
	65	Oil	-1,056	99	-11 ⑰
	55	Coal	11,988	568	21
3. Low Excess Air Plus Flue Gas Recirculation	70	Gas	1,998	293	7
	65	Oil	-276	99	-3
	55	Coal	6,642	568	12 ⑳
4. Flue Gas Scrubbing - $Mg(OH)_2$	--	Gas	--	--	--
	--	Oil	--	--	--
	80	Coal	33,040	826	40 Ⓒ

* From Section 4. (Table 4-5)

** From Section 8. (Appendix Tables)

*** 1000's of tons of NO_x emitted from Uncontrolled Boilers.

**** Circled symbols are priority indicators.

Table 9-27

Estimated Control Costs per Ton of NO_x Reduced
Total United States 250 MW Boilers - 3942 Hours/Year

Control Method	% NO_x Reduction*	Fuel Used	Cost Per Year $1000**	NO_x Reduction 1000's of Tons/Yr.	Contro Costs $/Ton
Uncontrolled (Base Case)	0	Gas	0	97.5***	0
	0	Oil	0	87.9***	0
	0	Coal	0	595.8***	0
1. Low Excess Air	33	Gas	-160	32	-5 ⑪****
	30	Oil	-792	26	-29 ③
	25	Coal	0	149	0 ⑬
2. Low Excess Air Plus Two-Stage Combustion	60	Gas	1,960	59	33 ㉖
	55	Oil	162	48	4 ㉒
	50	Coal	12,688	298	43
3. Low Excess Air Plus Flue Gas Recirculation	60	Gas	2,200	59	37
	55	Oil	270	48	6
	50	Coal	7,198	298	24 ㉓

* From Section 4. (Table 4-5)
** From Section 8. (Appendix Tables)
*** 1000's of tons of NO_x emitted from Uncontrolled Boilers.
**** Circled symbols are priority indicators.

Table 9-28

Estimated Control Costs per Ton of NO_x Reduced
Total United States 120 MW Boilers - 2190 Hours/Year

Control Method	% NO_x Reduction*	Fuel Used	Cost Per Year $1000**	NOx Reduction 1000's of Tons/Yr.	Control Costs $/Ton
Uncontrolled (Base Case)	0	Gas	0	77.5***	0
	0	Oil	0	87.9***	0
	0	Coal	0	586.8***	0
1. Low Excess Air	33	Gas	1,550	26.4	59 ㉔ ****
	30	Oil	-142	26.4	-5 ⑩
	25	Coal	5,214	146.7	36 ㉑
2. Low Excess Air Plus Two-Stage Combustion	53	Gas	9.920	41.9	237
	45	Oil	3,692	39.6	93
	40	Coal	34,128	234.7	145
3. Low Excess Air Plus Flue Gas Recirculation	53	Gas	6,200	41.9	148
	45	Oil	1,988	39.8	50
	40	Coal	19,434	234.7	83

* From Section 4. (Table 4-5)

** From Section 9. (Appendix Tables)

*** 1000's of tons of NO_x emitted from Uncontrolled Boilers.

**** Circled symbols are priority indicators.

The circled numbers in the last column of Tables 9-24 to 9-28 are listed in priority order from lowest cost control to highest cost control, for combustion modification. The circled letters A, B, and C indicate priority order for flue gas scrubbing control. Table 9-24 will be used to illustrate the logic which determines priority order for 1000 MW boilers. The lowest circled number in this table is number 4 for 1000 MW oil fired boilers, using low excess air plus two-stage combustion. Thus, this control method-boiler size-fuel combination offers the fourth lowest cost per ton of NO_x removed, among all of the practical combustion control combinations for all size power boilers. We should note that low excess air applied singly on this sized boiler would not be practiced, since combined low excess air plus two-stage combustion removes more nitrogen oxides at no additional cost. Similar logic holds for gas fired boilers. However, for coal fired 1000 MW boilers Table 9-24 indicates that the highest combustion control priority is low excess air, followed by low excess air plus flue gas circulation, and finally low excess air plus two-stage combustion. However, if flue gas scrubbing control is considered in competition with combustion control, the priority order among 1000 MW coal fired boilers would be first, low excess air and second, flue gas scrubbing.

Figure 9-5 illustrates graphically how priority orders were selected for composite 1000 MW coal fired boilers. Solid lines have been drawn for each of the four control methods with the slope of each line (cost per ton NO_x removed) shown numerically. Dashed lines are shown for other combinations of control methods. For example, the dashed line connecting LEA with $Mg(OH)_2$ indicates possible combinations of control methods, starting at the point labeled LEA with 100% of the 61 United States boilers controlled by LEA to the point $Mg(OH)_2$ indicating all 61 boilers controlled by $Mg(OH)_2$ flue gas scrubbing. The slope of this dashed line, -2.6, indicates the rate at which costs change with each ton of NO_x reduced. We can label this quantity, -2.6, as the "incremental substitution cost" for substituting $Mg(OH)_2$ control for LEA control. As pointed out later in this section, the order of incremental substitution cost quantities establishes the order in which controls are applied for the optimum cost effectiveness profile. If only combustion modification controls are considered, the optimum cost effectiveness profile segments would be LEA, LEA plus FGR, and finally LEA plus two-stage combustion. The final segment has a slope of $64.7 per ton NO_x removed, indicating the high cost of substituting two-stage combustion control for flue gas recirculation, when using low excess air.

Figure 9-6 presents cost effectiveness profiles of total United States power plants. Three minimum cost curves are shown. The lowest curve summarizes the minimum cost terminal points utilizing optimum combinations of combustion modification and flue gas scrubbing. The minimum cost path to reduce NO_x emissions by 6.4 million tons is shown as solid line segments running between squares. The minimum cost path utilizing combustion control only is shown as solid line segments running between solid circles.

Figure 9-5

COST EFFECTIVENESS PROFILES FOR 61 COMPOSITE 1000 MW COAL FIRED BOILERS

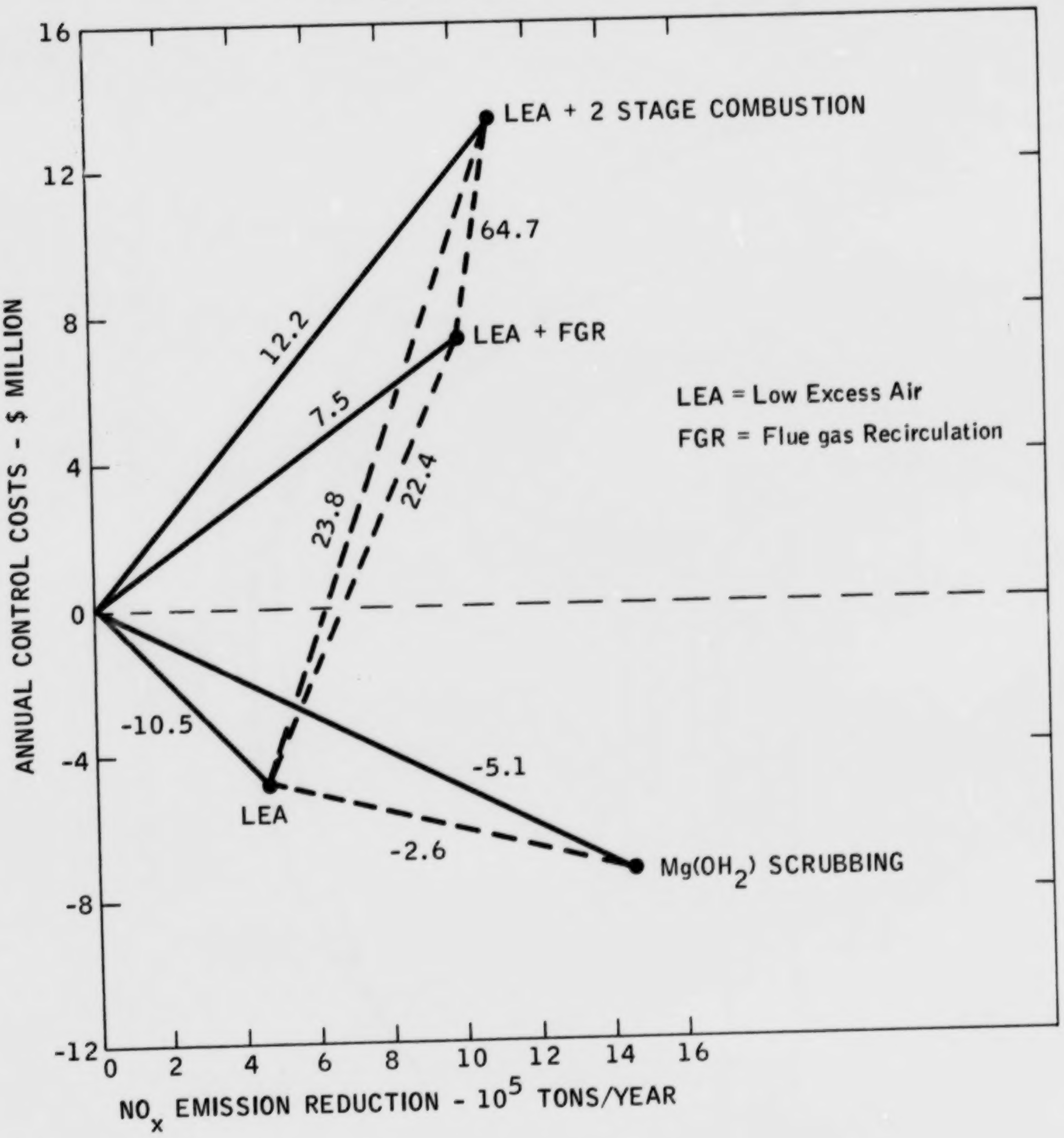
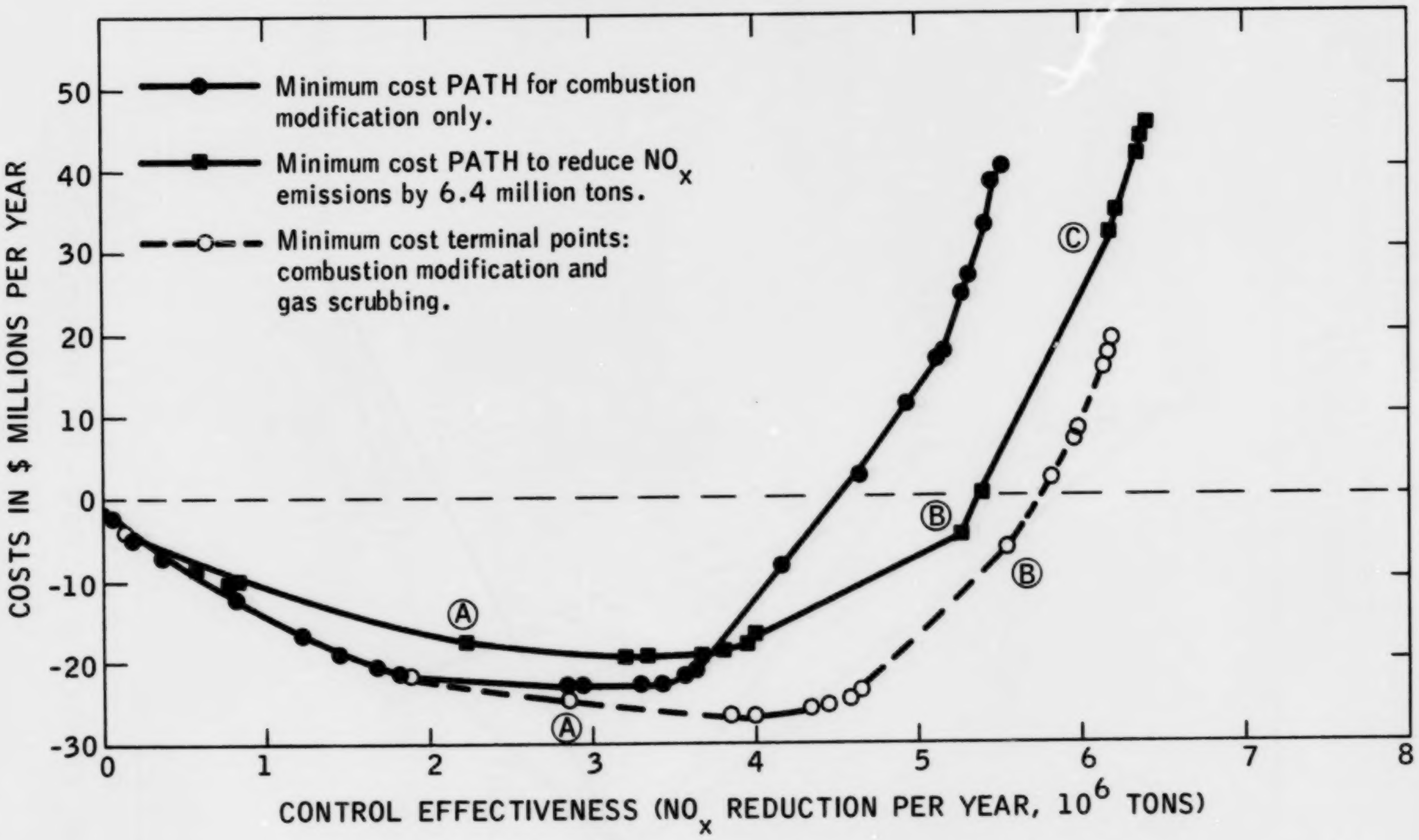


Figure 9-6

COST EFFECTIVENESS PROFILES -
UNITED STATES POWER PLANTS



The latter path passes through a minimum annual cost of -\$23 million (cost reduction) at 3 million tons NO_x reduction. Use of the optimum combination of flue gas scrubbing and combustion modification results in a minimum cost of -\$26 million at 4 million ton NO_x reduction. The optimum combination of power plant control at estimated zero costs results in NO_x reduction of about 5.7 million tons of NO_x per year. The points labeled A, B, and C indicate flue gas scrubbing control while all of the other points represent combustion modification controls.

Tables 9-29, 9-30, and 9-31 present the data plotted on Figure 9-6 listed in optimum priority order. Thus, in Table 9-29 it is seen that the first three steps along the minimum cost path use low excess air combustion control on oil fired boilers of 750, 500 and 250 MW capacity, respectively. The fourth step is low excess air plus two-stage combustion applied to 1000 MW boilers. The first step where incremental substitution costs are used to establish priority order occurs is step 14, low excess air plus two-stage combustion applied to 750 MW, gas fired boilers. In step 8, 750 MW gas fired boilers apply low excess air control at an estimated cost of \$-7.1 per ton of NO_x reduced. At step 14, two-stage combustion is added to these boilers at an estimated incremental cost of \$1.5 per ton of additional NO_x removed. Thus, the minimum path is comprised of minimum cost steps arranged in priority order of minimum cost per ton of NO_x removed at each step.

Table 9-30 presents the optimum order of control steps comprised of both combustion modification and flue gas scrubbing ($Mg(OH)_2$), to remove 6.4 million tons of NO_x. Comparing this path which includes flue gas scrubbing with the combustion modification only path indicates continuously lower total costs for reductions of more than 3.7 million tons of NO_x. For example, for a 5.4 million ton reduction, combustion modification only would cost over \$30 million per year compared to less than \$1 million per year when the minimum cost path to ultimately reach 6.4 million ton reduction is used. Table 9-31 indicates that the optimum combination of flue gas and combustion controls for 5.5 million ton reduction would result in estimated costs of \$-6.6 million. Thus, it is clear that the priority order of NO_x controls depends to some extent upon the ultimate NO_x reduction target. If the ultimate target is to be reached in more than one stage, the optimum control steps for each stage can be calculated by the methods used in developing Tables 9-29 through 9-31.

TABLE 9-29

MINIMUM COST PATH FOR COMBUSTION CONTROL ONLY - TOTAL U.S. POWER BOILERS

Boiler Size (MW)	Fuel Burned	Control Method	Control Cost ($/Ton)	Incremental Substitution Cost ($/Ton)	NO$_x$ Removed/Yr. (10^3 Tons)		Cost/Year ($1000)	
					Indiv.	Cumul.	Indiv.	Cumul.
1. 750	Oil	LEA*	-30.5		81	81	-2,486	-2,486
2. 500	Oil	LEA	-31.4		51	132	-1,594	-4,070
3. 250	Oil	LEA	-29.3		26	158	-792	-4,862
4. 1000	Oil	LEA + 2 St.**	-13.6		197	355	-2,673	-7,535
5. 1000	Coal	LEA	-10.5		458	813	-4,819	-12,354
6. 750	Coal	LEA	-10.5		398	1211	-4,189	-16,543
7. 500	Coal	LEA	-8.5		258	1469	-2,187	-18,730
8. 750	Gas	LEA	-7.1		221	1690	-1,564	-20,294
9. 500	Gas	LEA	-6.8		138	1828	-945	-21,239
10. 120	Oil	LEA	-5.4		26	1854	-142	-21,381
11. 250	Gas	LEA	-4.9		32	1886	-160	-21,541
12. 1000	Gas	LEA + 2 St.	-2.0	-2	954	2840	-1,900	-23,441
13. 250	Coal	LEA	0.0		149	2989	0	-23,441
14. 750	Gas	LEA + 2 St.	-1.8	2	569	3337	-1,035	-22,912
15. 750	Oil	LEA + 2 St.	-12.4	3	180	3436	-2,233	-22,659
16. 500	Gas	LEA + 2 St.	0.8	8	293	3591	343	-21,471
17. 500	Oil	LEA + 2 St.	-10.6	11	99	3640	-1,056	-20,943
18. 1000	Coal	LEA + FGR***	7.5	22	1007	4189	7,503	-8,621
19. 750	Coal	LEA + FGR	8.2	24	875	4666	7,171	-2,739
20. 500	Coal	LEA + FGR	11.7	29	568	4976	6,642	11,568
21. 120	Coal	LEA	35.5		147	5123	5,214	16,782
22. 250	Oil	LEA + 2 St.	3.4	43	48	5145	162	17,736
23. 250	Coal	LEA + FGR	24.2	48	298	5294	7,198	24,934
24. 120	Gas	LEA	58.9		26	5321	1.550	26.484
25. 1000	Coal	LEA + 2 St.	12.2	65	1098	5412	13,420	32,401
26. 750	Coal	LEA + 2 St.	13.5	71	955	5492	12,851	38,081
27. 250	Gas	LEA + 2 St.	33.3	81	59	5518	1,960	40,201

* LEA = Low Excess Air
** 2 St. = Two Stage Combustion
*** FGR = Flue Gas Recirculation

TABLE 9-30

MINIMUM COST NO_x CONTROL PATH TO 6.4 MILLION TONS NO_x REMOVAL - UNITED STATES POWER PLANTS

	Boiler Size (MW)	Fuel Burned	Control Method	Control Cost ($/Ton)	Incremental Substitution Cost ($/Ton)	NO_x Removed/Yr. (10^3 Tons)		Cost Per Year ($1000)	
						Indiv.	Cumul.	Indiv.	Cumul.
1.	750	Oil	LEA*	-30.5		81	81	-2,486	-2,486
2.	500	Oil	LEA	-31.4		51	132	-1,584	-4,070
3.	250	Oil	LEA	-29.3		26	158	-792	-4,862
4.	1000	Oil	LEA + 2 St.	-13.6		1971	355	-2,673	-7,535
8.	750	Gas	LEA	-7.1		221	576	-1,564	-9,090
9.	500	Gas	LEA	-6.8		138	714	-945	-10,044
10.	120	Oil	LEA	-4.4		26	740	-142	-10,186
11.	250	Gas	LEA	-4.9		32	772	-160	-10,346
A	1000	Coal	$Mg(OH)_2$**	-5.1		1464	2236	-7,437	-17,783
12.	1000	Gas	LEA + 2 St.	-2.0		954	3190	-1,900	-19,683
13.	250	Coal	LEA	0.0		149	3339	0	-19,683
14.	750	Gas	LEA + 2 St.	-1.8	2	569	3687	-1,035	-19,154
15.	750	Oil	LEA + 2 St.	-12.4	3	180	3786	-2,233	-18,901
16.	500	Gas	LEA + 2 St.	0.8	8	293	3941	243	-17,713
17.	500	Oil	LEA + 2 St.	-10.6	11	99	3989	-1,056	-17,185
B	750	Coal	$Mg(OH)_2$	10.0		1273	5262	12,730	-4,455
21.	120	Coal	LEA	35.5		147	5409	5,214	759
C	500	Coal	$Mg(OH)_2$	40.0		826	6235	33,040	33,799
22.	250	Oil	LEA + 2 St.	3.4	43	48	6257	162	34,753
23.	250	Coal	LEA + 2 St.	24.2	48	298	6406	7,198	41,951
24.	120	Gas	LEA	58.9		26	6432	1,550	43,501
26.	250	Gas	LEA + 2 St.	33.3	81	59	6459	1,960	45,621

* Combustion control abbreviations as in Table 9-29.

** $Mg(OH)_2$ = Flue gas scrubbing with aqueous $Mg(OH)_2$.

TABLE 9-31

MINIMUM COST NO_x CONTROL POINTS FOR COMBUSTION CONTROL AND FLUE GAS SCRUBBING - UNITED STATES POWER PLANTS

	Plant Size (MW)	Fuel Burned	Control Method	Control Cost ($/Ton)	Incremental Substitution Cost ($/Ton)	NO_x Removed/Yr. (10^3 Tons) Indiv.	NO_x Removed/Yr. (10^3 Tons) Cumul.	Cost Per Year ($1000) Indiv.	Cost Per Year ($1000) Cumul.
1.	750	Oil	LEA*	-30.5		81	81	-2,486	-2,486
2.	500	Oil	LEA	-31.4		51	132	-1,584	-4,070
3.	250	Oil	LEA	-29.3		26	158	-792	-4,862
4.	1000	Oil	LEA + 2 St.C.	-13.6		197	355	-2,673	-7,535
5.	1000	Coal	LEA	-10.5		458	813	-4,819	-12,354
6.	750	Coal	LEA	-10.5		398	1211	-4,189	-16,543
7.	500	Coal	LEA	-8.5		258	1469	-2,187	-18,730
8.	750	Gas	LEA	-7.1		221	1690	-1,564	-20,294
9.	500	Gas	LEA	-6.8		138	1828	-945	-21,239
10.	120	Oil	LEA	-5.4		26	1854	-142	-21,381
11.	250	Gas	LEA	-4.9		32	1886	-160	-21,541
A	1000	Coal	$Mg(OH)_2$	-5.1	-3	1464	2893	-7,437	-24,159
12.	1000	Gas	LEA + 2 St.C.	-2.0		954	3847	-1,900	-26,059
13.	250	Coal	LEA	0.0		149	3996	0	-26,059
14.	750	Gas	LEA + 2 St.C.	-1.8	2	569	4344	-1,035	-25,530
15.	750	Oil	LEA + 2 St.C.	-12.4	3	180	4443	-2,233	-25,277
16.	500	Gas	LEA + 2 St.C.	0.8	8	293	4598	243	-24,089
17.	500	Oil	LEA + 2 St.C.	-10.6	11	99	4647	-1,056	-23,561
B	750	Coal	$Mg(OH)_2$	10.0	19	127	5522	12,730	-6,642
20.	500	Coal	LEA + F.G.R.	11.7	29	568	5832	6,642	2,187
21.	120	Coal	LEA	35.5		147	5949	5,214	7,401
22.	250	Oil	LEA + F.G.R.	3.4	43	48	6001	162	8,355
23.	250	Coal	LEA + F.G.R.	24.2	48	298	6150	7,198	15,553
24.	120	Gas	LEA	58.9		26	6176	1.550	17.103
26	250	Gas	LEA + 2 St.	33.3	81	59	6203	1,960	19,223
C	500	Coal	$Mg(OH)_2$	40.0	102	826	6461	33,040	45,621

* All abbreviations as in Table 9-30.

9.6 COST EFFECTIVENESS PROFILES OF NO_x CONTROL FOR MAJOR COMBUSTION SOURCES AND NITRIC ACID PLANTS IN THE UNITED STATES

In this section, a detailed cost effectiveness profile is calculated for maximum practical NO_x control of combustion and nitric acid plant sources in the United States for the year 1980. This profile is then used to establish the priority order for R&D planning in Section 10.

In addition to power plants discussed above, other known emission sources including pipelines, gas plants, industrial boilers, nitric acid plants, and refinery engines are included in this analysis. Effectiveness (Section 4) and costs (Section 8) for these additional sources have been analyzed in this section in the same manner as for power boilers, discussed above in detail. The minimum cost profile has been calculated for the optimum combination of controls for NO_x reduction from stationary sources up to a total of about 9 million tons of NO_x. An arbitrary maximum control cost of \$103/Ton of NO_x reduction was established as a practical limit for applying control. Since our estimates indicated that the cost-effectiveness of NO_x control for domestic combustion sources would range between \$2000 and \$4000 per ton of NO_x removed (based on a modest cost of \$20 per unit for modifications), this emission source category was excluded from the nationwide cost-effectiveness analysis. For localized situations the sum total of these low level emissions may be a problem which would have to be solved eventually. It is important to emphasize that the costs and effectiveness data assumed for the year 1980 are based upon successful research and development followed by control application based on optimized practice.

Table 9-32 lists 39 control steps included in calculating the cost-effectiveness profile shown in Figure 9-7. Since cost savings are estimated for many of these control steps, (principally low excess air), the optimum combination of controls will reduce a significant portion of total stationary NO_x emissions at little or no cost. For example, a 4.2 million ton NO_x reduction can be obtained at an estimated cost saving of \$26.5 million per year, or 7.5 million ton NO_x reduction can be obtained at an estimated annual cost of less than \$.4 million per year. Table 9-33 below summarizes NO_x reductions and costs for three NO_x emission reduction targets: a "high" target of 8.9 million tons, a "medium" target of 7.5 million tons and a "low" target of 4.2 million tons.

Table 9-33

Control Costs for Three U.S. NO_x Emission Reduction Targets

Emission Source	NO_x Emission Reduction Targets								
	8.9 million Tons-"High"			7.5 million Tons -"Medium"			4.2 million Tons - "Low"		
	NO_x Reduction (10^3 Tons)	Annual Cost (\$$10^6$)	\$/Ton	NO_x Reduction (10^3 Tons)	Annual Cost (\$$10^6$)	\$/Ton	NO_x Reduction (10^3 Tons)	Annual Cost (\$$10^6$)	\$/Ton
Power Boilers	6,460	44.1	7	5,522	-6.6	-1	3,996	-26.1	-7
Pipelines	1,370	4.4	3	1,370	4.4	3	0	--	--
Gas Plants	405	2.6	6	405	2.6	6	0	--	--
Industrial Boilers	326	6.1	19	181	-0.5	-3	181	-0.5	-3
Nitric Acid	259	14.3	55	0	--	--	0	--	--
Refinery Engines	65	.7	11	62	0.5	8	25	0.03	1
Total	8,886	72.2	8	7,540	0.4	0.1	4,202	-26.5	-6

Table 9-32

Minimum Cost NO_x Control Points
United States Combustion and Nitric Acid Plant Sources

Emission Source	Fuel Burned	Control Method	Control Cost ($/Ton)	Incremental Substitution Cost ($/Ton)	NO_x Removed/Yr (10^3 Tons) Indiv.	NO_x Removed/Yr (10^3 Tons) Cumul.	Cost Per Year ($1,000) Indiv.	Cost Per Year ($1,000) Cumul.
750 MW	Oil	LEA	-30.5		81	81	-2,486	-2,486
500 MW	Oil	LEA	-31.4		51	132	-1,584	-4,070
250 MW	Oil	LEA	-30.0		26	158	-792	-4,862
1000 MW	Oil	LEA + 2 St.	-13.6		197	355	-2,673	-7,535
1000 MW	Coal	LEA	-10.5		458	813	-4,819	-12,354
750 MW	Coal	LEA	-10.5		398	1,211	-4,189	-16,543
500 MW	Coal	LEA	-8.5		258	1,469	-2,187	-18,730
145 WT	Oil	LEA	-8.0		47	1,516	-376	-19,106
750 MW	Gas	LEA	-7.1		221	1,737	-1,564	-20,670
500 MW	Gas	LEA	-6.8		138	1,875	-945	-21,615
120 MW	Oil	LEA	-5.4		26	1,901	-142	-21,757
250 MW	Gas	LEA	-5.0		32	1,933	-160	-21,917
1000 MW	Coal	$Mg(OH)_2$	-5.1	-2.6	1,464	2,940	-7,437	-24,535
1000 MW	Gas	LEA + 2 St.	-2.0		954	3,894	-1,900	-26,435
188 WT	Coal	LEA	-1.2		57	3,951	-70	-26,505
145 WT	Gas	LEA	-0.6		78	4,029	-47	-26,552
250 MW	Coal	LEA	0.0		149	4,178	0	-26,552
1800 R.E.	Gas	H2O Inj.	1.2		25	4,203	31	-26,521
750 MW	Gas	LEA + 2 St.	-1.8	1.5	569	4,551	-1,035	-25,992
1800 G.P.	Gas	H_2O Inj.	1.9		159	4,710	305	-25,687
750 MW	Oil	LEA + 2 St.	-12.4	2.6	180	4,808	-2,233	-25,434
Pipeline	Gas	H_2O Inj.	3.2		1,370	6,178	4,422	-21,012
500 MW	Gas	LEA + 2 St.	-0.8	7.7	293	6,333	243	-19,824
300 G.P.	Gas	H_2O Inj.	9.3		246	6,579	2,280	-17,544
500 MW	Oil	LEA + 2 St.	-10.6	10.8	99	6,628	-1,056	-17,016
300 R.E.	Gas	H_2O Inj.	13.0		38	6,666	488	-16,528
750 MW	Coal	$Mg(OH)_2$	10.0	19.3	1,273	7,541	12,730	391
HNO_3	New	2 Stage	27.0		114	7,655	3,086	3,477
500 MW	Coal	LEA + FGR	11.7	28.5	568	7,965	6,642	12,306
120 MW	Coal	LEA	35.5		147	8,112	5.214	17,520
36 WT	Coal	LEA	37.7		78	8,190	2,960	20,480
250 MW	Oil	LEA + 2 St.	43.4		48	8,212	162	21,434
250 MW	Coal	LEA + 2 St.	48.3		298	8,361	7,198	28,632
28 WT	Oil	LEA	53.9		67	8,428	3,590	32,222
120 MW	Gas	LEA	58.9		26	8,454	1,550	33,772
300 R.E.	Gas	H_2O Inj.	72.0		3	8,457	219	33,991
HNO_3	Old	2 Stage	77.2		145	8,602	11,186	45,177
250 MW	Gas	LEA + 2 St.	33.3	80.6	59	8,628	1,960	47,297
500 MW	Coal	$Mg(OH)_2$	40.0	102.3	826	8,886	33,040	73,695

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KEY:

750 MW -- 750 Megawatt Power Boiler
145 WT -- 145,000 lb. st/hr Water Tube Boiler
1800 R.E. -- 1800 HP Refinery Engine
1800 G.P. -- 1800 HP Gas Plant Engine
HNO3 -- Nitric Acid Plant

* All abbreviations as in Table 9-30.

Figure 9-7

COST EFFECTIVENESS PROFILE - NO_x CONTROL FOR MAJOR UNITED STATES EMISSION SOURCES

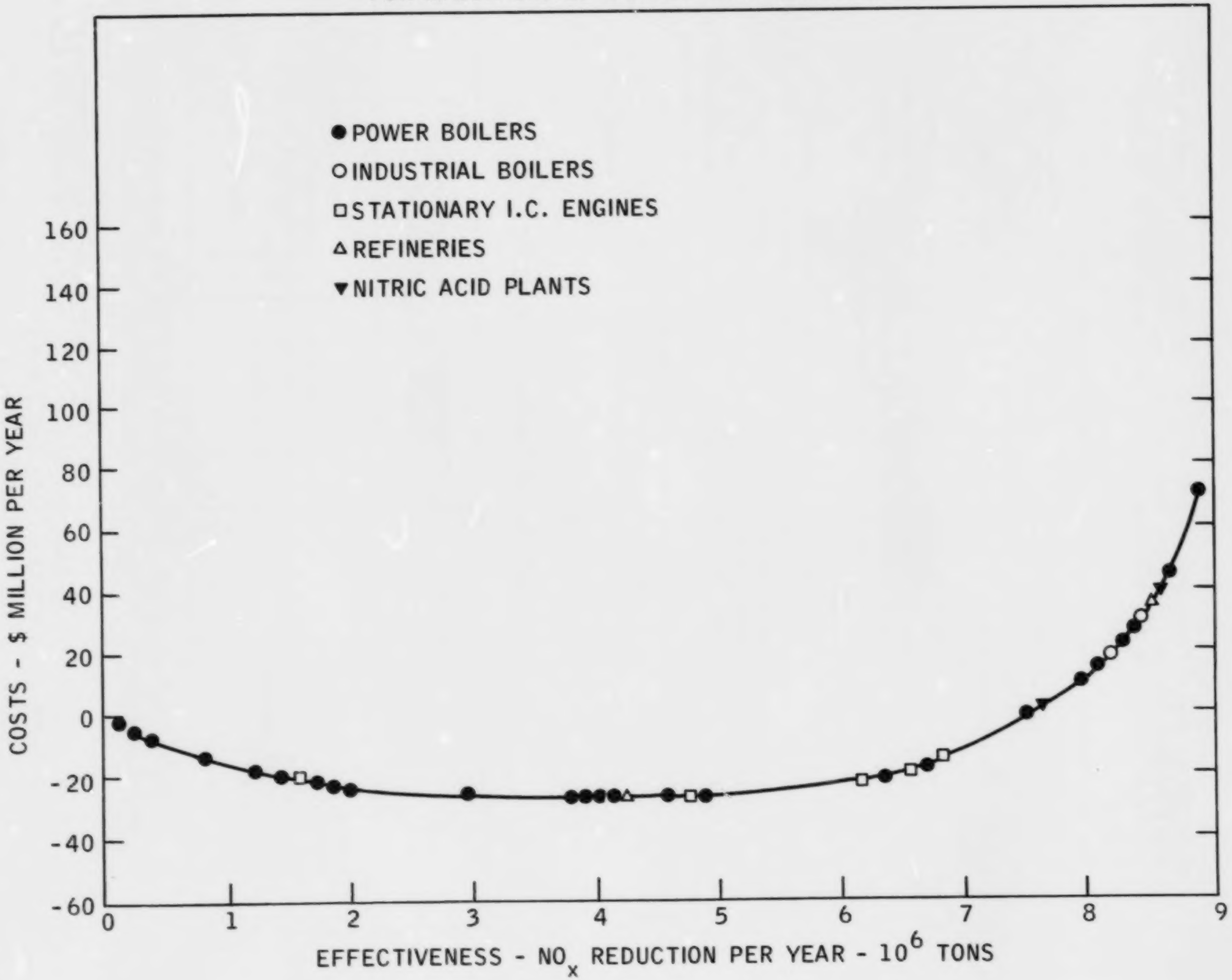


Table 9-33, which summarizes most of the essential information contained in the more detailed Table 9-32, can be used to establish control method priorities in a logical manner. Starting first with a "low" cost target of 4.2 million ton NO_x reduction, it is readily apparent that the highest priority should be power boilers with a potential annual cost savings of \$26 million per year. Industrial boilers would be second priority and refinery engines last. Note that no controls would be applied to the other sources if the optimum combination of controls were applied to achieve this "low" target. Examining the "medium" target of 7.5 million tons NO_x reduction, it is seen that power boilers with \$6.6 million annual savings have the highest priority followed by industrial boilers. Based upon cost-effectiveness criterion (\$/Ton NO_x reduction), the remaining source control priorities would be in the order of first, pipelines; next, gas plants; and finally, refinery engines. If the "high" target was established as an objective, all controls methods would have to be successfully achieved. Based exclusively on cost effectiveness criteria, the priority order would be pipelines, gas plants, power boilers, refinery engines, industrial boilers and finally, nitric acid plants. However, recognizing the fact that most pipeline and gas plant emissions occur in relatively remote geographic regions, a more practical priority order considering both criteria would be power boilers, refinery engines, industrial boilers, piplines, gas plants and finally nitric acid plants. Table 9-34 below lists these ranks established above for ready comparison.

Table 9-34

Priority Rankings by NO_x Emission Source

	"Low" Target	"Medium" Target	"High" Target	Overall Priority Order
1. Power Plants	1	1	3	1
2. Pipelines		3 (Remote)	1 (Remote)	4
3. Gas Plants		4 (Remote)	2 (Remote)	5
4. Industrial Boilers	2	2	5	2
5. Nitric Acid			6 (Spot)	6
6. Refinery Engines	3	5	4	3

The priority order of emission control techniques applied to the emission sources above are listed below:

Source	Priority Order of NO_x Control Methods
Power Plants	(1) LEA, (2) LEA + 2 St. C., (3) $Mg(OH)_2$, (4) LEA + FGR.
Industrial Boilers	(5) LEA,((10) LEA + FGR)
Refinery Engines	(6) Water injection
Pipelines	(7) Water injection
Gas Plants	(8) Water injection
Nitric Acid Plants	(9) Two Stage Combustion

Figure 9-8 indicates the estimated nitrogen oxide emission for the U.S. from stationary sources over the period 1950 to 2000. The top curve in the figure assumes no further controls beyond those already in use in the 1960's. The other three curves are derived assuming the three levels of control discussed above.

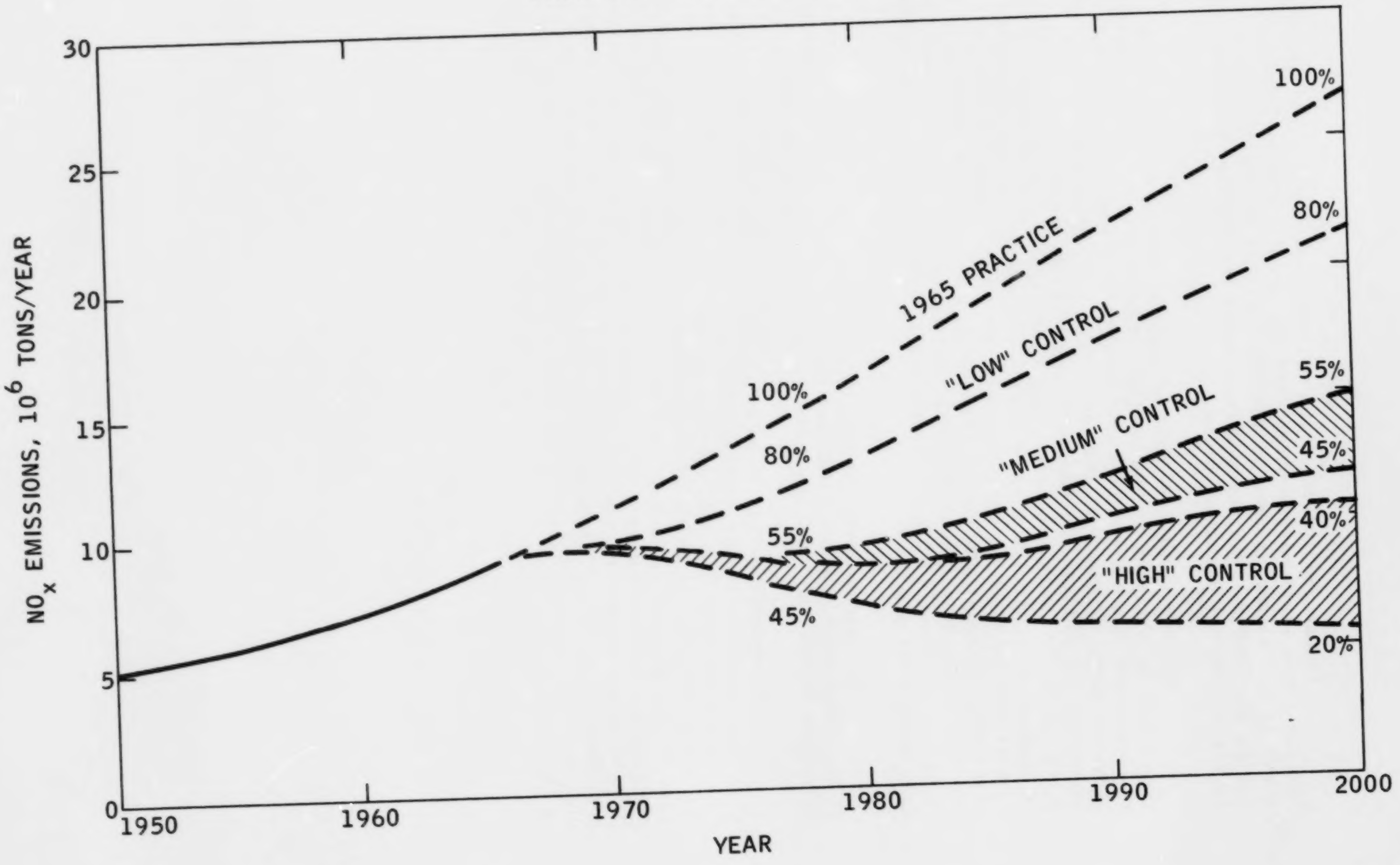
The curve labeled "medium" control target indicates the results that would be obtained if the optimum combination of controls were applied to combustion sources to the point that total annual control costs were close to zero. Table 9-32 indicates that for 1980 a breakeven point occurs at 7.5 million ton NO_x reduction with an annual cost of \$390 thousand. These estimated costs are based upon successful research and development of combustion control methods (chiefly low excess air and two-stage combustion) followed by optimized application to power boilers and large stationary internal combustion engines (water injection control). For the year 2000, we estimate that "medium" control levels could reduce NO_x emissions to about 45-55% of the potential emissions which would result from using 1965 practices.

The lowest curve labeled "high" control target is our estimate of the range within which potential control techniques would reduce NO_x emissions if all the controls shown in Table 9-32 were applied.

To summarize this section briefly, it should be noted that NO_x emissions from stationary sources using a "low" level of control are estimated to have increased from 5.2 million tons in 1950 to 9.0 million tons in 1965 and would increase to about 13 millions tons in 1980 and over 21 million tons in the year 2000. Due to the favorable economics of some control procedures, we have forecast that potential NO_x emissions can be ideally reduced to about half of the 1965 practice emissions at about breakdown cost levels. A "high" level of control is estimated to reduce 1980 potential emission by over 50%, and the year 2000 potential emissions to close to the 1950 level.

Figure 9-8

POTENTIAL CONTROLLED NO_x EMISSIONS
FROM U.S. STATIONARY SOURCES



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10. R&D PLANS ON STATIONARY NO_x EMISSION CONTROL

In this section of the report, program items having definite R&D requirements are discussed. The basis of these R&D plans developed for the National Air Pollution Control Administration is the cost-effectiveness analysis of existing and potential NO_x control methods presented in Section 9.

The stationary NO_x R&D program items are divided into the following major categories.

I. Combustion process studies.

II. Combustion flue gas treatment studies.

III. Non-combustion process studies.

IV. Supporting studies dealing with other aspects of the NO_x problem.

Within the above categories, individual program items are discussed, again subdivided into logical basic research and applied R&D requirements. Following the discussion of the specific R&D plans, the program plans are ranked in order of priorities from the standpoint of potential accomplishments, i.e., the maximum effectiveness accomplished at minimum cost. This ranking is presented in the form of priority blocks.

By choosing alternative paths in the formulation of the 5-year R&D plans, the strategy of execution and corresponding funding of individual program items may be accomplished within the framework of a coordinated system. Depending on the level of funding available to NAPCA for the implementation of the R&D plans, specific program items or blocks may be accelerated or delayed, without creating situations where information would be lacking for the continuation of critical studies aimed at solving the major problems in stationary NO_x control.

In addition to the strategic ranking of R&D priorities, rough cost estimates have also been generated for the implementation of the program plans.

Based on the assessment of existing and potential control technology, NAPCA should be in a position to implement the five-year plans detailed below, with the expectation that the R&D work will culminate in a considerable reduction of the stationary NO_x emissions.

10.1 COMBUSTION R&D

The characterization of the stationary NO_x emission problem has shown that over 95% of "man-made" emissions emanate from fossil fuel combustion sources. Also, based on the cost-effectiveness assessment of control methods, combustion modification techniques appear to be the most promising from the standpoint of technical and economic attractiveness, and the potential accomplishments which may be achieved.

In this section, the R&D plans related to combustion modification techniques are detailed. First, the basic research requirements for an improved understanding of the phenomena influencing NO_x formation in combustion processes are discussed. These studies are recommended as a necessary adjunct to the development of optimized combustion modification techniques. In the second part of this discussion of combustion R&D, the necessary applied program items are detailed.

10.1.1 Basic and Supporting Research

This section deals with combustion research required to provide presently lacking information necessary for NO_x control via optimizing combustion modification techniques. There is a natural feed-back of information, respectively, among the basic program items designed to fill gaps in our present knowledge, their application to actual combustion equipment, and the codification of all pertinent basic factors into a mathematical model capable of guiding the design of low NO_x and other pollutant emitting combustion equipment. Thus, we shall first discuss the R&D work recommendation on the basic aspects of the "combustion system."

10.1.1.1 Kinetic Studies of NO_x Formation and Decomposition under Combustion Conditions

This program consists of basic laboratory studies, under carefully designed combustion conditions. Most of our present information on NO_x kinetics are based on idealized studies of NO formation and decomposition in the absence of combustible species, and free radicals resulting from the oxidation of combustibles.

A wide range of fuel/air ratios, varying from substoichiometric air supply to various excess air levels must be used to obtain representative kinetic information. In particular, the concentration and role of oxygen atoms and hydroxyl radicals in the NO_x kinetics should be defined with special emphasis on combustion conditions with substoichiometric air supply.

Clearly, the work should start with the combustion system most readily amenable to detailed, quantititive investigation. This is the combustion of gaseous (natural gas or vaporized hydrocarbons) fuel with air. Thus,sophisticated instrumental methods, e.g., spectroscopy, may be applied to determine not only the ultimate concentration of NO_x in combustion gases, but also, to measure the concentration of intermediates involved in the detailed kinetic mechanism.

As these studies progress, the work should be extended to the combustion of fuel oil sprays and coal particles, with their attendant problems of atomization, vaporization, volatilization, and burning rates, respectively.

The complexities introduced by burning fossil fuels containing organically bound nitrogen, fuel oil and coal, also require detailed kinetic investigation. It is felt that initial experiments should be conducted with "doped" fuels under idealized conditions, i.e., pure hydrocarbons with representative nitrogen compound types added. The broad categories of nitrogen compound types found in fuel oils are the so-called "basic" and "non-basic" types. A systematic selection representing such nitrogen compounds, and in addition the less frequently found amines, should be used in these studies. The kinetics of fuel nitrogen oxidation, the intermediate species, and the ultimate fate of fuel nitrogen should be determined. Based on the results obtained in the above manner, actual fuel systems will be investigated over a range of fuel nitrogen compound composition, concentration, and combustion conditions.

The pertinent kinetic information obtained in the above studies will provide new or improved input data for the refinement of the first-generation mathematical model.

10.1.1.2 Flame Probing in Representative Combustion Equipment

While limited data are available on the final NO_x emissions from combustion equipment of various sizes, as affected by operating and design features, very little is known about the development of NO_x (and other pollutant species) profiles in combustors.

The studies recommended to fill this gap in available information should consist of probing the combustion zone under well defined conditions, in systematically selected combustion equipment ranging from small domestic burners to power plants. Temperature-concentration profiles should be determined both axially and radially, with equipment consisting of movable shielded thermocouples and water-cooled, quenched aspirating sample probes. These studies will entail the selection of appropriate probing equipment, its design and construction, combined with the selection of the best available wet chemical or instrumental methods of chemical analysis. Ideally, continuous NO_x monitoring equipment should be used. However, if current instrumentation is not available, future research is necessary to develop such instrumentation.

As stated above, not only temperature and NO_x profiles, but concentration profiles for unburned fuel, carbon monoxide generated, and other components of combustion gases should be established. It is envisioned that a significant portion of this type of fundamental information, necessary for an improved understanding of the factors affecting NO_x formation may be carried out in conjunction with the research recommended in Section 11.1.2.1 on the application of known combustion modification methods to selected equipment in a systematic study. These investigations will also produce new, or improved NO_x emission factors for various types of combustion equipment fired with gas, oil or coal fuels.

10.1.1.3 Kinetic Modeling of NO_x Formation and Decomposition in Combustion Processes

A first-generation mathematical model has been formulated and used at Esso for predicting the rate of NO_x formation and decomposition in natural gas combustion processes during Phase I of the stationary NO_x systems study. This model has been shown capable of predicting directional effects of combustion modification techniques, such as low excess air firing, two-stage combustion, and flue gas recirculation. However, in its present form, the model is applicable only to fuel-lean conditions (due to the lack of appropriate kinetic data), and neglects the effects of mass, momentum, and heat transport within the combustion zone.

Further extensions to this model should incorporate additional kinetics, based on the laboratory and flame probing studies outlined above. Also, transport effects should be incorporated, using mixing models, including the effects of fuel/air distribution and internal recirculation.

The model should be extended to the combustion of fuel oil spray droplets and coal particles. This work should entail the incorporation of droplet size distribution functions, rates of atomization, and evaporation, and droplet burning rates for fuel oil, as well as the rate of volatilization and carbon burning rates for coal fuel particles.

These models should be subjected to continuous refinement, based on the availability of new data generated in NAPCA's proposed program on NO_x emission control, and also, from all newly published literature sources. The use of realistic burning rates will allow the determination of the effect of NO_x control methods on other pollutant species, specifically unburned fuel and carbon monoxide. Again, refined kinetics input is required for the modeling studies.

As the mathematical modeling work progresses, its predictions should be compared with actual laboratory and test data. After these refinements, the final version of the NO_x mathematical model will be useful for formulating optimum combustion modification techniques for the design of low NO_x emitting combustion equipment.

10.1.2 Applied R&D

As discussed above, the ideal way of planning R&D work on combustion modifications for NO_x control is to set up a "feedback" cycle between basic and applied studies. The applied R&D program recommendations for the broad application of combustion modification methods which should result in the potentially highest degree of NO_x control are summarized in this section.

10.1.2.1 Systematic Study of Proven and Potential Combustion Modification Methods for Power Plant Boilers

The cost-effectiveness analysis of NO_x control methods has shown that the control of emissions from power plant boilers has the highest priority on the basis of potential pollutant reductions. The present systems study representing Phase I of NAPCA's program aimed at stationary NO_x emission control methods has identified combustion modification techniques with definite potential for the broad-based control of NO_x emissions from fossil fuel fired power plants.

A systematic experimental design is required to define the applicability of known combustion modification techniques to populations of power plants of various sizes and having different design features, burning different fossil fuel types. Such a program must be designed in cooperation with the owners and operators of the equipment, and the work should be phased according to the probability of successful applications of NO_x control.

Thus, representative boilers must be selected, using, for example, front-wall, opposed-wall, and tangential firing with gas, oil and coal fuels. The combustion modification techniques which have been identified in this study are low excess air firing, two-stage combustion, flue gas recirculation, steam or water injection, and most important, the combination of these methods.

For oil and gas fired installations, arrangements should be made to test all known techniques in an attempt to define their range of applicability, and optimize NO_x emission control. The test work must be carried out using standardized sampling and analytical procedures (again agreed upon with the owners and operators of the combustion equipment), in order to establish general validity for the results obtained. For coal-fired installations, a similar approach should be taken, and with a more restricted scope of full-scale testing, based on the very real difficulties faced by attempts to modify coal combustion for NO_x control. The "coal problem" is of such a magnitude and importance, that it should be approached with a full awareness of potential difficulties. Therefore, a separate program item (10.1.2.2) is recommended over and above the testing program included for coal in this section.

To optimize combinations of combustion modification methods for NO_x control, full advantage should be taken of the new findings uncovered during the test program itself, and of the combined results of laboratory and NO_x modeling studies. It is anticipated that for each class of power plant furnaces, fired with the three types of fossil fuels, novel optimized combinations will result in later phases of this program.

All of the testing studies discussed above must be accompanied by thorough data, engineering, and economic evaluations. This approach will provide the complete framework of this crucial phase of the R&D program on stationary NO_x control.

10.1.2.2 Development and Testing of Combustion Modifications for Coal Firing

The program plan recommended to tackle the coal combustion problem (which on a nationwide basis represents the bulk of NO_x emissions for power plants) consists of three phases:

1. Limited testing work with full-scale equipment, to define the applicability and constraints of techniques such as low excess air firing, two-stage combustion and flue gas recirculation.

2. Parallel with full-scale testing, laboratory and pilot-scale studies should be initiated. The laboratory work should be addressed to basic combustion problems with coal in connection with NO_x emissions, while the pilot-scale studies are recommended for a greater degree of flexibility in the application of combustion modification methods than available in full-scale equipment. For example, careful counter-measures can be thus applied against explosive hazards resulting from fuel/air imbalances and flame-out, while the economic risks due to malfunction or corrosive damage to equipment may be minimized.

3. As the most applicable combustion modification techniques are defined by laboratory and pilot plant studies, these methods should be tested in their optimized versions with full-scale equipment. At the end of this program item, combustion modification methods should be available to provide the optimum degree of NO_x control for coal-fired equipment.

10.1.2.3 Study of Applicability of Combustion Modification Techniques in Intermediate and Small Scale Equipment

The cost-effectiveness analysis of the NO_x control problem has shown a significant incentive to control emissions from intermediate size boilers. On the other hand, even assuming a highly optimistic degree of control, and minimal expenditures to modify small, domestic combustion equipment, this latter category appears to be relatively unimportant.

The philosophy of designing a test program on combustion modification methods for intermediate boilers is similar to that used for large utility boilers in program item 10.1.2.1. Based on cost-effectiveness, low excess air firing and flue gas recirculation (and possibly two-stage combustion for very large packaged boilers) have been shown to be the most attractive control methods.

A systematic selection of equipment according to operating and design features is required at the start of the program. The tests should be coordinated with owners and operators of such equipment (including manufacturers). As combustion modification techniques are tested, engineering evaluations will be required to define equipment problems, solutions, and the economical degree of applicability of the methods tested.

In the sector of small combustion equipment, essentially a "breakthrough" is required for a novel type of combustion device which would emit low levels of NO_x. This may be possible, in the future, by combining very high heat release and removal rates. As shown by the technical appraisal of the factors affecting NO_x emissions from combustion processes (Sections 4.2 and 4.3), this type of combination would kinetically limit the formation of NO_x. Fluid bed combustion of natural gas may be applicable in this category.

As regards the **application** of "known" combustion modification methods to small combustion equipment for NO_x control, the incentives to carry out R&D in this area are indeed very low.

10.1.2.4 Combustion Modification for NO_x Emission Control from Stationary Internal Combustion Engines

The characterization of the stationary NO_x problem has shown that on a nationwide basis, stationary internal combustion engines, used primarily as gas compression drivers, rank second only to fossil fuel burning boilers in NO_x emissions. However, the overwhelming majority of these stationary I.C. engines are in locations remote from major population centers (pipelines and gas plants), so that the relative lack of exposure of densely populated areas to such emissions mitigates, to some extent, against the actual mass of NO_x emitted by these sources.

Nonetheless, on a long range control planning basis, it is reasonable to operate under the assumption that emissions from these sources will have to be controlled. As discussed in Section 9, cost-effectiveness analyses of the NO_x emission problem and its potential control, assign a definite priority to the development of stationary I.C. engines (mainly gas engines) NO_x emission controls.

For the 5-year R&D plan, it is recommended that the first phase of this program item should concern itself with emission control problems which are common to stationary and vehicular I.C. engines. In other words, only incremental funding is envisioned to direct attention to the NO_x emission problem from stationary engines. This emission control area is actually simpler than that for motor vehicles, because variable driving speed conditions are not applicable, and load variations are less frequent. On the basis of cost-effectiveness, water injection, and possibly flue gas recirculation show a rather attractive potential. The advantage of a close tie-in with the motor vehicle emission control program is that even those technical areas, which from the point of view of cost-effectiveness do not appear attractive enough to be pursued in the stationary R&D program, (e.g., catalytic decomposition or selective reduction of NO_x) will be followed closely for potential breakthroughs.

In the second phase of the stationary I.C. engine control programs, engine and field testing of applicable methods should be conducted. The work should include gasoline and gas engines, as well as gas turbines. The objective of these studies should be to validate the work carried out with test engines or automobiles for application of NO_x emissions control to the various types of stationary I.C. engines.

10.1.2.5 Study of NO_x Formation and Control in Novel Combustion Systems

Fluidized bed combustion is a novel technique under development, as discussed in Section 4.4.2.3 of this report. While the low bed temperatures (1600-1800°F) limit the formation of NO via the direct reaction of O_2 and N_2, chemically bound nitrogen in the fuel is oxidized to NO_x.

Because of the attractive features of fluid bed combustion (very high heat transfer rates and potential control of SO_2 emissions through the use of additives), it is felt that currently funded programs should also be focused on potential NO_x control. This may be accomplished through the use of additives which tend to decompose the NO formed (limestone is known to have such catalytic activity in the temperature range of fluidized bed combustion), or by operating under two-stage combustion conditions. In the first stage, the fluidized bed could be supplied with substoichiometric quantities of air, and it is possible that under such reducing conditions NO_x may form only in small concentrations. The unburned fuel should be oxidized to complete burnout in a second fluid bed combustion stage with the addition of excess air. If feasible, the second stage should be integrated with the first stage.

Separate engineering and economic evaluations of the feasibility of fluid bed combustion with gas fuel are also required. Gas contains negligible amounts of combined nitrogen, so that NO_x formation can be minimized. If this concept is economically feasible, the fluid bed combustion technique is recommended for evaluation through laboratory, pilot plant and prototype demonstration studies in the five-year R&D program.

Similar considerations apply to other novel combustion systems which offer the advantage of very high heat transfer rates. Packed beds may be used potentially to accomplish "flameless" combustion, due to the high rates of heat removal. Under such conditions, as in the case of fluid bed combustion, neither thermodynamic equilibrium, nor kinetic rates would favor the formation of NO_x.

Advanced and "exotic" electric power-generation cycles should be carefully scrutinized from the standpoint of NO_x formation and emission control. This program sector should also include the use of treated and converted fuels, which may contain chemically bound nitrogen. As regards "exotic" power generation cycles, none of these have advanced to the point that actual experimental studies of NO_x control should be made. Magnetohydrodynamic electric generation, which has a somewhat cloudy outlook, could be potentially operated in a two-stage combustion scheme, to minimize NO_x formation. Alternately, the very high temperatures reached in MHD generate such high concentrations of NO_x that flue gas treatment processes with byproduct recovery may be attractive. However, widespread application of MHD generation, which is regarded unlikely for the time period considered, could conceivably saturate the byproduct market. These developments should be followed closely in Phase II of the stationary NO_x control study, but no direct experimentation is recommended at this time.

10.2 COMBUSTION FLUE GAS TREATMENT R&D

The prime consideration for R&D recommendations to study the removal of NO_x from combustion flue gases is that both NO_x and SO_2 emissions must be controlled by such processes. The cost-effectiveness analysis of such methods has shown that flue gas treatment for NO_x control alone is impractical.

Flue gas treatment, although requiring much greater capital investments than combustion modification techniques, shows a definite potential for NO_x and SO_2 emission control for coal or oil fired installations. Even with byproduct credits, only a few approaches appear to be attractive enough on the basis of cost-effectiveness, and these techniques are recommended for detailed study in the five-year R&D program. The fact that combustion modification techniques may have only limited applications to coal-firing provides additional impetus for the development of economically feasible flue gas treatment processes.

As a cautionary, but important note, all flue gas treatment processes should be investigated with real flue gas (i.e., gases containing all components of flue gases), to avoid potential pitfalls.

10.2.1 Basic Research

Basic laboratory studies are needed to help develop effective flue gas treatment processes. These studies should be aimed at providing quantitative information as a function of operating parameters, as well as the understanding of fundamental phenomena which may promote or limit the applicability of flue gas treatment techniques for NO_x control.

10.2.1.1 Gas Phase Interactions

The cost-effectiveness analysis of NO_x control methods has shown that aqueous scrubbing of flue gases (with recycle of NO_2 to achieve equimolar NO-NO_2 concentrations) has an attractive potential for NO_x/SO_2 emission control.

The success of developing aqueous scrubbing methods depends, in part, on the gas phase interactions of flue gas species. Specifically, NO_2 is reduced by SO_2 into NO, and the competition between this reaction and the absorption of equimolar mixtures of NO/NO_2 may seriously affect the feasibility of the process. A detailed investigation is recommended to study rates of absorption as affected by gas phase concentrations of NO_2, NO, SO_2, O_2, temperature, pressure, and other reaction and operating parameters.

10.2.1.2 Liquid Phase Interactions

Basic laboratory studies on the liquid phase interactions affecting aqueous scrubbing systems are recommended in conjunction with the investigation of gas phase interactions. The interactions of bisulfite, sulfite, sulfate, nitrite and nitrate anions must be sorted out before an aqueous scrubbing process could be developed.

Absorption rate measurements are required in various alkaline scrubbing solutions, e.g., $Mg(OH)_2$, $Ca(OH)_2$, NaOH (the $Mg(OH)_2$ system appears to be the most attractive for controlling both SO_2 and NO_x emissions, based on the cost-effectiveness assessment.) The effects of absorption conditions, e.g., temperature, pH of the solution, nature and concentration of the metal ions should be determined quantitatively in these studies.

10.2.1.3 Catalysis of NO Decomposition

To date, no promising catalyst system has been developed which would be capable of decomposing flue gas NO into N_2 and O_2 at practical rates, under net oxidizing conditions.

Based on the cost-effectiveness analysis of potential NO_x control methods, the chances of success for an economically attractive development in this area appear quite remote. However, laboratory studies are being carried out for the control of automobile exhaust NO_x emissions. For this reason, it is recommended that in the stationary NO_x control R&D program, the developments in automobile exhaust emission control should be followed, but no direct R&D work is recommended in this area for flue gas emission control.

10.2.1.4 Catalysis of Selective NO Reduction

Essentially, the same comments apply as for section 10.2.1.3. Some interesting exploratory developments have been reported on the selective reduction of NO (in the presence of O_2) with CO or H_2. However, at reasonable catalyst costs and flue gas space velocities, this approach does not seem to be attractive enough for R&D work aimed at flue gas NO_x emission control.

10.2.1.5 Catalysis of NO Oxidation

This program item is related to the development of aqueous scrubbing processes for NO_x/SO_2 control. If the technical potential of aqueous scrubbing techniques with NO_2 recycle for equimolar NO/NO_2 sorption can be established, higher rates of NO oxidation to NO_2 would be desirable. A research study in this area is recommended in the five-year R&D program.

10.2.2 Applied R&D

As discussed earlier, the studies recommended on the basis of cost-effectiveness analysis in the area of NO_x emission control by combustion flue gas treatment are directed towards the control of both NO_x and SO_2 pollutant emissions.

"Applied R&D," as the term is used here, does not involve large-scale tests of as yet undeveloped processes. It simply means that these studies are oriented toward specific process applications, rather then dealing with the acquisition of necessary fundamental information. As emphasized before, the simulation of realistic conditions is paramount in these studies, i.e., the flue gas treatment processes must be investigated using real flue gas, to render the results meaningful.

10.2.2.1 Absorption of NO_x in Aqueous Alkaline Solutions

The absorption of equimolar amounts of NO and NO_2 in aqueous alkaline solutions has been identified by the Esso NO_x Systems Study as a category of flue gas treatment processes with high priority. While unattractive for gas-fired installations, the conceptual process using aqueous $Mg(OH)_2$ solution as the sorbent shows outstanding potential for coal and oil fired power plants.

Due to the lack of available information, a systematic study of aqueous alkaline solutions is in order. Typical examples are the aforementioned magnesium hydroxide system, but scrubbing with lime water and caustic should also be included in the initial investigations.

Absorption rate data must be obtained under realistic conditions over a broad range of characteristic process parameters. These should include the NO/NO_2 ratio in the flue gas, pH and temperature of the sorbent solution, gas velocity, cation concentration, among others. An important variable to determine is the nitrite/nitrate distribution in the spent (or partially spent) sorbent. The oxidation of nitrites to nitrates would be undesirable from the standpoint of recovering NO by sorbent regeneration.

The most attractive aqueous sorbent system is recommended for study under pilot-scale and prototype demonstration conditions for NO_x/SO_2 control. The process studies, if shown feasible, must be accompanied by careful engineering and economic evaluations to define the scope of the process, and optimize its applicability.

10.2.2.2 Aqueous Sorbent Solution Regeneration Studies

Regeneration of the aqueous sorbent is a necessary part of the overall study designed to develop the best aqueous sorbent system for flue gas treatment.

These studies (including engineering evaluations) should include the evaluation of known methods of regenerating the sorbent:

- Thermal methods (particularly attractive for minimizing the heat load with aqueous $Mg(OH)_2$ as the sorbent, as the nitrite can be decomposed under pressure, without prior evaporation).
- Acidification to release NO.
- Electrodialysis using bipolar membranes for continuous acidification.

As part of these studies, sorbent life should also be determined to narrow down the selection of sorbents. Ultimately, if these studies are successful, a complete "process package" should result, which may be built into new designs, or retrofitted to existing power plant installations. Under favorable conditions, the byproduct credits associated with flue gas treatment may offset the cost of air pollution control, or even yield a profit.

10.2.2.3 NO_x Scrubber Performance and Efficiency Studies

High scrubber efficiency is a prerequisite for the development of a successful sorbent process for NO_x/SO_2 control. As discussed in Section 9.2 the cost of flue gas treatment involving NO_2 recycle may sky-rocket as scrubber efficiency decreases over a relatively narrow range for the Tyco Laboratories-type modified lead chamber acid process. Since this process utilizes NO_2 for the oxidation of SO_2 to SO_3 to make sulfuric acid, high NO_x scrubber efficiency is imperative.

Although less sensitive to scrubber efficiency, aqueous alkaline scrubbing processes are also subject to limitations imposed by scrubber performance and efficiency, for reasons of process economics.

The definition of scrubber performance for such systems is imperative. This factor is regarded as a top priority item in the flue gas treatment area of the five-year R&D program.

10.2.2.4 NO_x Adsorption With Solids

Certain solid sorbents have been identified as having technical potential for combustion flue gas treatment to control NO_x emissions. Manganese dioxide and alkalized ferric oxide are candidates based on published information.

In spite of their potential attractiveness, solid sorbents suffer from the very serious limitation of sorbent attrition problems. Until some indications are shown in the flue gas desulfurization area of the NAPCA program (or through new leads) that attrition problems may be overcome, the development of solid sorbent systems for NO_x control is not recommended.

10.2.2.5 Solid Sorbent Attrition and Regeneration Studies

The same comments apply as for Section 10.2.2.4. Unless solid sorbent systems are uncovered which can demonstrate attrition resistance in flue gas treatment applications, no R&D programs are recommended.

10.2.2.6 Evaluation of Applicability of Flue Gas Desulfurization Processes Under Development to NO_x Control

Some flue gas desulfurization processes have the potential of NO_x control as well. Chief among these is the modified lead chamber acid process being studied by the Tyco Research Laboratories. Another flue gas desulfurization process study, also sponsored by NAPCA, is the Princeton Chemicals Research low pressure Claus process. The latter, at least based on thermodynamic equilibrium considerations, may have the potential of selective reduction of NO_x with H_2S to yield sulfur as the byproduct.

As discussed in this report, the Tyco-type process is critically dependent on scrubber efficiency. If the studies recommended under Section 10.2.2.3 validate this approach, incremental funding of the on-going studies is recommended for NO_x control. The work should, under favorable circumstances, culminate in the development of a low cost (or possibly profit-making) combined desulfurization-NO_x control process.

To date, the NO_x control potential of the low pressure Claus process has not been demonstrated. Incremental funding is recommended to explore the potential of this approach for NO_x control.

In addition to the above studies, it is recommended that all on-going or future flue gas desulfurization studies should be oriented to incorporate the assessment of their potential for flue gas NO_x removal. If favorable results develop, the level of effort should be stepped up in future studies.

10.3 ECONOMIC EVALUATION OF OTHER MEANS OF LIMITING URBAN EXPOSURE TO NO_x EMISSIONS

The Esso Systems Study has established that the nationwide NO_x emission problem is the composite of individual "pockets" of urban-metropolitan area exposures to high levels of NO_x in the atmosphere. Because of the very high rates of natural emissions of NO_x, the man-made pollution sources have a lesser impact on less populous areas, due to atmospheric dilution mechanisms. An exception is, of course, the "local nuisance" problem created by very high level spot emissions of NO_x, e.g., in chemical processing plants manufacturing or using nitric acid.

One (at least temporary) approach to alleviate urban exposure to NO_x emissions is to locate sources such as fossil fuel power plants or nitric acid plants in remote locations. These measures are, of course, quite sensitive to the economics of electric power transmission costs, or in the case of chemical plants, raw material and finished product shipment costs and the availability of other utilities and manpower.

For the electric utility industry, the advances made in reducing the cost of long distance transmission have made it possible to generate power from mine-mouth locations in some cases. The "four-corners" location is a good illustration for supplying electrical energy to the Los Angeles area, without contributing to the severe air pollution problem of that chronically affected area.

Continuing economic and engineering evaluations are recommended to evaluate the applicability of the "remote location" approach to alleviating the urban NO_x emission problem.

Nuclear generation is, of course, a solution for eliminating NO_x emissions resulting from power generation. While forecasts vary, the impact of nuclear generation will undoubtedly be quite large by the year 2000. From the process control engineering standpoint, however, these developments are recommended only for close scrutiny to orient NAPCA's program planning, but not as part of the five-year R&D plan.

10.4 ENGINEERING AND ECONOMIC ANALYSIS OF AVAILABLE NO_x CONTROL METHODS FOR PLANTS MANUFACTURING AND USING NITRIC ACID

The assessment of control technology dealing with NO_x emissions from nitric acid manufacturing or uses (Sections 6.1 and 6.2) shows that control methods are available. The solution of this problem hinges on the economic factors of chemical manufacturing, particularly for processes using nitric acid.

Clearly, there is an incentive to eliminate the "local nuisance problems" associated with nitric acid. Based on the cost-effectiveness evaluation of the contribution of this sector to the overall problem, it is recommended that case-by-case engineering and economic studies should be carried out, to determine the applicability of available control techniques to individual plants. It would be beneficial, if such studies could be carried out in cooperation with chemical process industry companies and government operated plants manufacturing and using nitric acid.

10.5 R&D PROGRAM SCHEDULES, COSTS AND PRIORITIES

A descriptive tabulation of all recommended R&D program items for stationary NO_x emission control is given in Table 10-1. These program items have been divided into three broad areas:

- Basic Research (denoted by "B")
- Applied R&D (denoted by "A")
- Supporting Studies (denoted by "S").

Within each of these areas, the individual program items are arranged in a related sequence of 5-year R&D plan recommendations. In the formulation of Table 10-1, closely related programs appear following each other. However, the individual program items interact in complex, multiple ways. These interactions are shown graphically in Figures 10-1, 10-2 and 10-3. The need for efficient exchange and feed-back of information is clear from the interactions of basic, applied and supporting study program items. Close coordination of the implementation of the 5-year R&D plans is recommended, including the continuing review and updating these plans. This approach will ensure the most efficient utilization of R&D funding allocated by NAPCA for this problem area.

Funding requirements for the implementation of all recommended program items have been estimated. These R&D cost estimates are shown in Table 10-2. To provide maximum flexibility for implementing the R&D plans, depending on the level of funding available, the program items and costs have been ordered into five "priority blocks". The implementation of each of these R&D priority blocks can be started at different times, as dictated by priority-funding requirements.

The priorities have been arrived at by considering the potential accomplishments based on carrying out the individual program items, and also the interdependence of continuing studies aimed at controlling NO_x emissions from major sources. In other words, this assignment of priorities is a direct consequence of the cost-effectiveness analysis of NO_x control methods discussed in Section 9.

Clearly, the most important stationary NO_x emission source sector is fossil fuel burning power plants. The Priority 1 program items are largely addressed to the reduction of NO_x emissions from these sources. Again, based on the cost-effectiveness analysis, other major contributing sectors are included in the program plans, according to their potential impact. These have been arranged as a function of the funding available to carry out coherent studies with well-defined end objectives.

The estimated costs for the recommended 5-year R&D programs range from about \$3.6 million (if only Priority 1 items are included), to an upper level of about \$12 million for the entire program. It should be emphasized that these cost estimates do not include the participation required by

Table 10-1

Basic Research Programs

Program Designation	Program Year 1	2	3	4	5
1B	NO_x Kinetic Modeling in Combustion Extend and Improve Present Model By: --incorporating new kinetic data --incorporating heat, mass and momentum transport effects --vaporization, volatilization and burning rates of oil and coal --treating combustion modifications by direct programming	--incorporate additional new kinetic data generated by 2B --incorporate kinetic data on fuel N generated by 2B --compare model results with lab data 2A and boiler tests 1A --predict optimized combustion modification techniques and use to test concepts	--continue evaluation of new concepts --update and finalize model --test against newest lab and plant data --prepare final computer program (and deck) for general use		
2B	Define NO_x Kinetics in Combustion --study mechanism of NO formation and decomposition under rich and lean combustion conditions --generate improved NO formation and decomposition rate data --study role of organically bound fuel nitrogen on NO formation defining effects of compound type and combustion conditions	} → --obtain kinetic data on fuel nitrogen oxidation			
3B	Determine Temperature and Concentration Profiles in Actual Boilers as Affected By: --design parameters --fuel type --method of operation	Develop improved and novel furnace and boiler designs and concepts --define their potential and problems --make preliminary engineering and cost assessments			

Table 10-1 (Continued)

Basic Research Programs

Program Designation	Program Year 1	2	3	4	5
4B		Laboratory Investigation of Means of Improving Coal Combustion for NO_x Control --determine effect of particle size --air/fuel ratio --coal injection and distribution	} →		
5B			Laboratory Studies to Investigate Problems Arising from Applied Combustion Modification Studies. Requires very close tie into 1A	→	
6B	Determine Basic Factors Affecting Aqueous Scrubbing Systems --gas phase interactions of NO, NO_2, SO_2, O_2 --liquid phase interactions of HSO_3^-, $SO_3^=$, SO_4^-, NO_2^-, NO_3^- with each other and NO_2, SO_2, O_2 --effectiveness of different alkaline scrubbing solutions for NO_x removal	→ + NO oxidation studies			
7B	Define design and operating parameters required for achieving high scrubber efficiencies essential to Tyco-type process				

Table 10-1(Continued)

Applied Research and Development Programs

Program Designation	Program Year 1	2	3	4	5
	Combustion				
1A	Systematic Combustion Modification Study in Power Plant Boilers				
	• Oil & Gas Fired Boilers --Study low excess air, 2-stage combustion flue gas recirculation and combinations of these techniques on a range of boiler types and sizes --Study burner modifications alone, and in combination with above	→	Complete testing of oil and gas fired boilers		
	• Coal Fired boilers --Limited tests on lower excess air operation and on flue gas recirculation	Apply completely tested pilot plant combustion modifications to full-scale testing of coal fired boilers	Test other combustion modification techniques in full scale coal fired boilers. Include combined fuel firing	Complete testing of coal fired boilers →	
	• Develop sampling and analytical procedures				
2A	Pilot scale studies on effects of low excess air, 2-stage combustion and flue gas recirculation and burner design with emphasis on coal combustion	→ Study dual-fuel combustion including overfiring coal with gas or oil	→ Complete pilot plant studies		

Table 10-1(Continued)

Applied Research and Development Programs

Program Designation	Program Year 1	2	3	4	5
3A		Engineering, Applicability and Cost Studies of Combustion Modification Techniques for Power Plants. Highlight problems in low excess air, 2-stage combustion flue gas recirculations for: --Modifying existing boilers --Design of new boilers	Develop detailed engineering drawings, specification sheets and cost estimates for combustion modification techniques proven effective	→	
4A	Emphasize NO_x control in on-going fluidized bed combustion studies	Experimental studies on aspects of fluidized bed combustion shows attractive for NO_x control --N-free fuels --use of specific additives --two-stage combustion of coal --combustion of oil, gas, treated or converted fuels	→	Modify existing prototype fluidized bed combustion unit to evaluate experimentally proven techniques	Test prototype and produce evaluation of process
5A		Include analysis of above technique in engineering and economic studies directed at fluidized bed combustion of coal (for SO_2 control)			Final engineering and economic analysis of fluidized bed combustion technique
6A	Review and assess application of automotive NO_x emission control techniques to stationary internal combustion engine	Laboratory testing of applicable combustion modification techniques for stationary gas internal combustion engine Continue appraisal of new developments in automotive emission control	Full-scale field testing of combustion modification techniques for stationary gas internal combustion engines	→ + engineering evaluation of technology	

Table 10-1 (Continued)

Applied Research and Development Programs

Process Designation	Program Year 1	2	3	4	5
7A			Apply findings of basic (1-4B), and applied combustion studies (1-3A) on NO control to a range of intermediate boilers of varying size, design and fuel. Analyze results	→ + Start studies on small combustion sources	→ + Engineering evaluation of control techniques for intermediate and small combustion sources
8A	Limited testing of equimolar NO/NO_2 absorption in existing prototype aqueous scrubbing systems being evaluated for SO_2 control	Pilot plant studies with best alkaline aqueous scrubbing systems (from 6B), probably $Mg(OH)_2$. Study absorption, regeneration of sorbent and oxidation of NO	→	Design and construction of a prototype aqueous scrubbing system for combined SO_x-NO_x emission control	Prototype testing; obtain data needed for full engineering evaluation of process
9A			Engineering studies of best aqueous alkaline scrubbing system		Engineering and economic evaluation of prototype results
10A		Continue pilot plant development of sulfuric acid scrubbing process if scrubber efficiency studies (7B) indicate high efficiencies can be obtained in commercial process at reasonable costs.	Move sulfuric acid scrubbing to prototype stage if pilot scale studies are promising Costs borne entirely by SO_2 area budget from here on	→	
11A	Review and Update Current Pollution Control Programs to Include Consideration of NO_x Control • Fuel Conversion Research --determine fate of organic nitrogen --fuel quality studies from standpoint of NO_x producing tendency				

Table 10-1 (Continued)

Applied Research and Development Program

Program Designation	Program Year 1	2	3	4	5
	• Advanced Power Cycles --combined gas-steam cycles --Exotic power cycles (MHD, etc.) • Plume dispersion and stack meteorology • Flue gas desulfurization processes - review for potential for NO_x control • Incineration studies • Urban exposure prevention --remote location --nuclear generation	Experimental studies on novel SO_2-NO_x control techniques	Most of further funding from SO_2 control R&D funds with partial support from 12A		
12A	Studies of combustion modification or flue gas control techniques that evolve	→	→	→	→
13A	Engineering and economic studies of applicability of existing and potential NO_x control methods to specific plants manufacturing and using nitric acid. Program aimed at aiding manufacturers	→	→		
14A	Review new chemical process developments from standpoint of NO_x abatement	→	→		

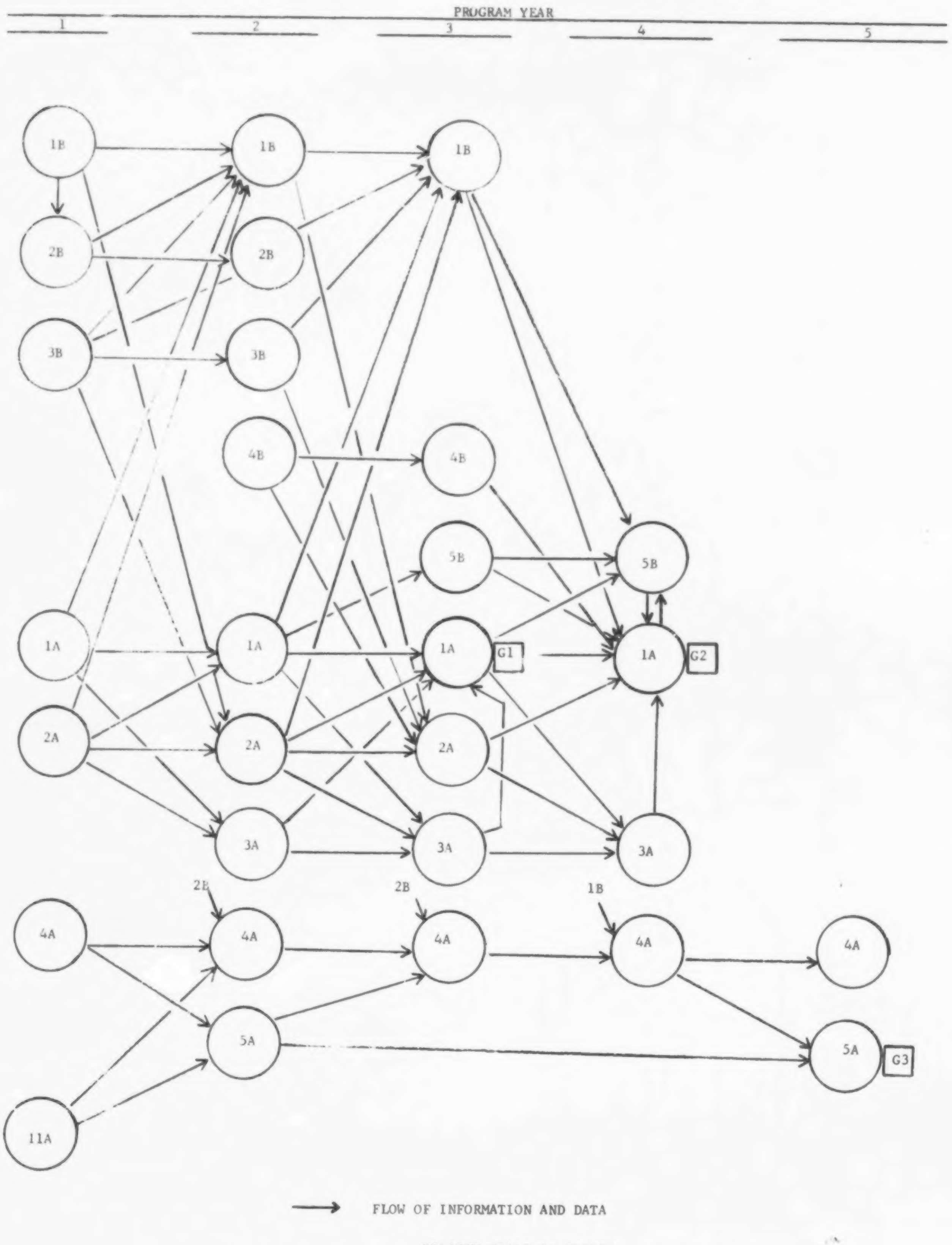
Table 10-1(Continued)

Supporting Studies

Program Designation	1	2	3	4	5
1S	NO_x Analytical Methods Assessment --assess current methods --define gaps and approaches to better analysis (Use information developed under Contract CPA 22-69-154 as starting point)	Develop improved analytical methods	Refine developments and subject to field trials		
2S	Fill NO_x Emission Factor Gaps	Continue for Power Plants as Part of 1A	→	→	
	Develop improved factors for boilers as a function of design, operating and fuel parameters (Include as part of 1A)	Develop improved factors for other combustion sectors (industrial boilers, process heaters, residential, stationary engines, etc.)	Develop improved factors for remaining combustion and new combustion sectors (HNO_3 plants, etc.)		
3S	Updating of Total Program and Reassessment of Stationary NO_x Problem	→	→	→	→

FIGURE 10-1

INTER-RELATION OF 5-YEAR NO_x CONTROL PROGRAM PLAN ITEMS; COMBUSTION MODIFICATION PROCESSES FOR POWER PLANT FURNACES

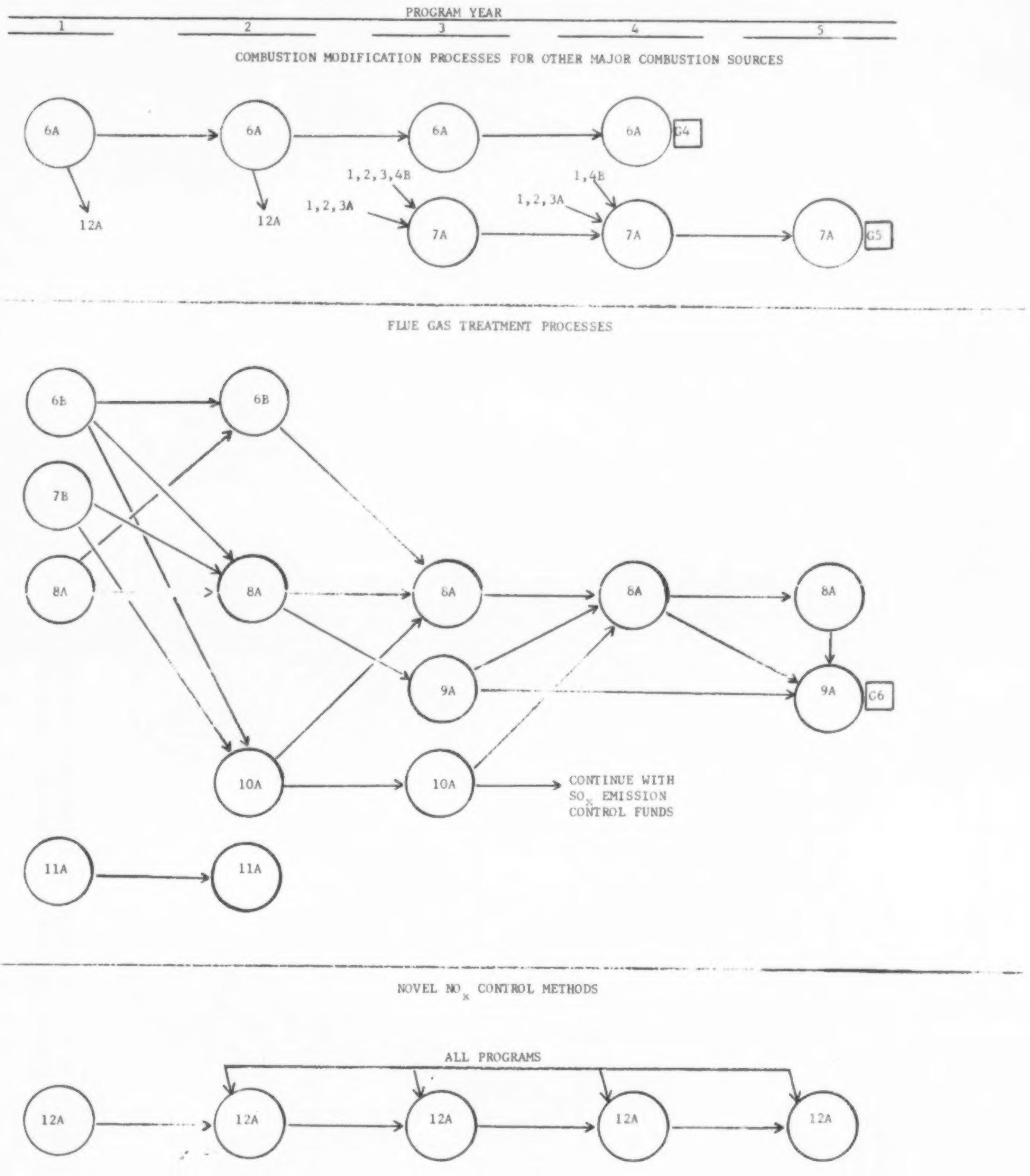

PROGRAM YEAR
1
2
3
4
5
1B
2B
3B
1B
2B
3B
4B
1B
4B
5B
5B
1A
2A
1A
2A
3A
1A
G1
2A
3A
1A
G2
3A
2B
2B
1B
4A
4A
4A
4A
4A
5A
5A
G3
11A
FLOW OF INFORMATION AND DATA

PROGRAM GOALS COMPLETED

G1 - 1ST GENERATION CONTROL DEVELOPED FOR GAS AND OIL FIRED POWER PLANTS.
G2 - 1ST GENERATION CONTROL DEVELOPED FOR COAL FIRED POWER PLANTS.
G3 - LOW NO_x FLUIDIZED BED COMBUSTOR DEVELOPED.

FIGURE 10-2

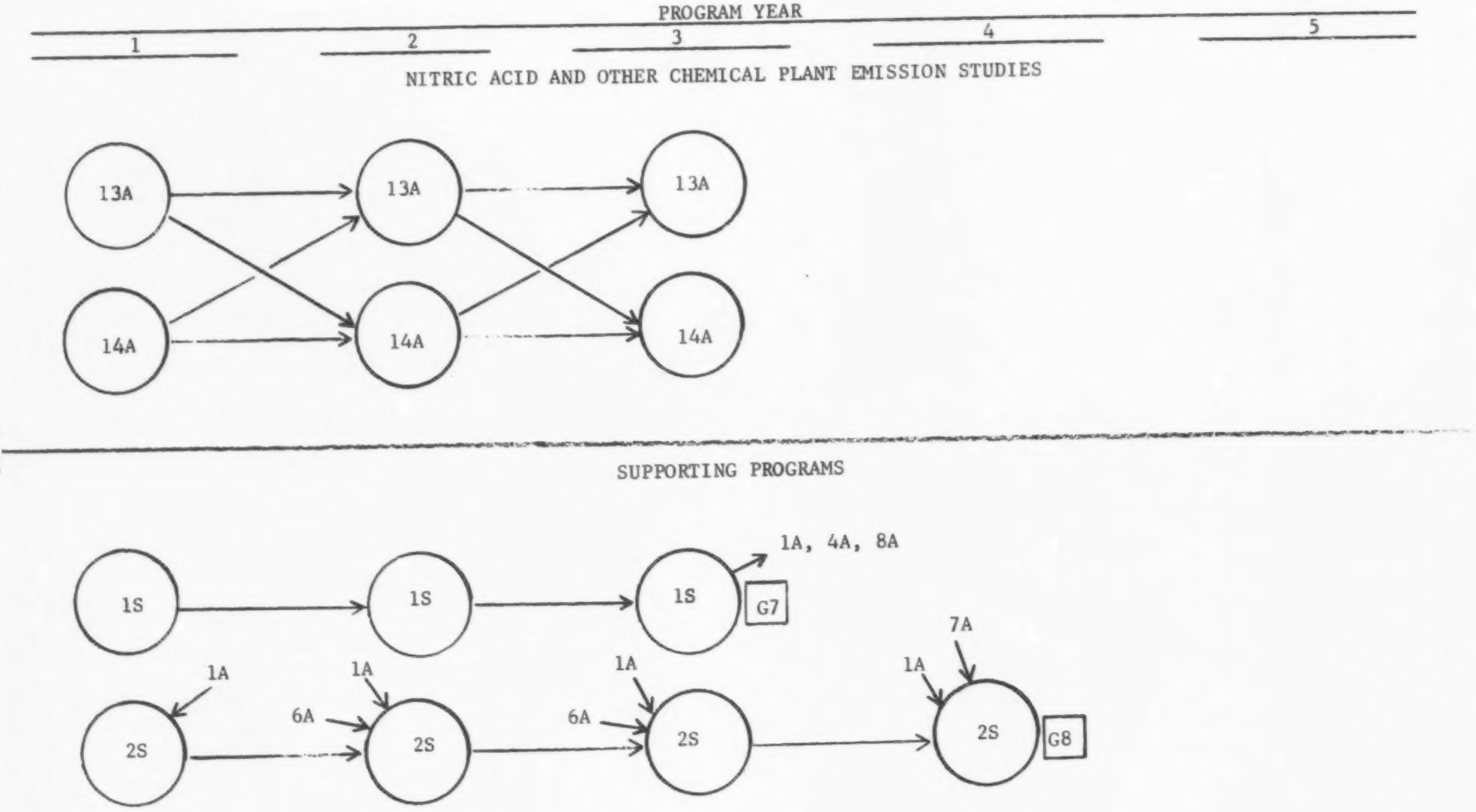
INTER-RELATION OF 5-YEAR NO_x CONTROL PROGRAM PLAN ITEMS


PROGRAM YEAR
1
2
3
4
5
COMBUSTION MODIFICATION PROCESSES FOR OTHER MAJOR COMBUSTION SOURCES
6A
12A
1,2,3,4B
1,2,3A
7A
1,4B
G4
G5
FLUE GAS TREATMENT PROCESSES
6B
7B
8A
9A
10A
11A
G6
CONTINUE WITH SOx EMISSION CONTROL FUNDS
NOVEL NOx CONTROL METHODS
ALL PROGRAMS

G4 - 1ST GENERATION CONTROL OF STATIONARY I.C. ENGINES AVAILABLE.
G5 - 1ST GENERATION CONTROL OF INTERMEDIATE AND SMALL COMBUSTION SOURCES ESTABLISHED.
G6 - AQUEOUS FLUE GAS SCRUBBING SYSTEM FOR NO_x/SO_2 CONTROL DEVELOPED.

FIGURE 10-3

INTER-RELATION OF 5-YEAR NO_x CONTROL R&D PROGRAM PLAN ITEMS


PROGRAM YEAR
1
2
3
4
5
NITRIC ACID AND OTHER CHEMICAL PLANT EMISSION STUDIES
13A
13A
13A
14A
14A
14A
SUPPORTING PROGRAMS
1S
1S
1S
1A, 4A, 8A
G7
1A
2S
1A
6A
2S
1A
6A
2S
7A
1A
2S
G8

G7 IMPROVED ANALYTICAL NO_x MEASUREMENT TECHNIQUES GENERATED.
G8 DEVELOPMENT OF IMPROVED NO_x EMISSION FACTORS COMPLETED.

TABLE 10-2

R & D PROGRAM PRIORITIES AND COSTS

Priority of Program Blocks	Program Item Designation*	Program Costs; 1,000 $ Year from Start of Individual Program Items 1	2	3	4	5	Totals
1	1 B	120	120	60			300
	2 B	100	150				250
	5 B			100	150		250
	1 A	150	200	350	400		1,100
	7 A			400	300	250	950
	9 A			50		50	100
	1 S	20	100	80			200
	3 S	50	100	100	100	80	430
	Total	440	670	1,140	950	380	3,580
2	3 B	80	100				180
	6 B	100	75				175
	2 A	250	250	100			600
	3 A		150	150	75		375
	Total	430	575	250	75	0	1,330
3	4 B		125	125			250
	7 B	50					50
	4 A	50	200	200	700	500	1,650
	6 A	50	100	250	250		650
	8 A	50	175	150	1,000	500	1,875
	12 A*	75	150	300	500	800	1,825
	Total	275	750	1,025	2,450	1,800	6,300
4	5 A		75			100	175
	10 A		150				150
	11 A	200	100				300
	Total	200	325	0	0	100	625
5	13 A	50	50	50			150
	14 A	25	25	25			75
	2 S		75	50			125
	Total	75	150	125	0	0	350
	Grand Total	1,420	2,470	2,540	3,475	2,280	12,185

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* See Table 10-1 for program description.

cooperating electric utility companies, boiler manufacturers, and other owners of operating combustion equipment that will be needed in these studies. Rough estimates of such additional cost requirements for this type of participation (primarily by power plants) range from a minimum of about \$7 million to a high of \$19 million, depending on the scope of field evaluation and validation tests made. This would result in total five-year program costs ranging from about \$10.6 million to \$31 million. Furthermore, an overall contingency of about 25% appears reasonable to allow for unpredictable program delays, disappointments and some duplication of effort which may be required.

11. LITERATURE SURVEY

An important starting point for the systems study was to assemble a set of about 3000 references and abstracts from the literature on NO_x and related topics. A fairly liberal selection of references was made, including basic information and background material through 1968 and highlights of the literature to September, 1969. The initial information collected was particularly useful for the parts of the project relating to statistical trends and control technology.

The strategy used for the literature review was to start with evaluated information from sources readily available, to get the best references as promptly as possible into the working files. The first step was to prepare a card file of some 400 references accumulated at the start of the project by the six members of the study team. These were derived from their previous knowledge and initial contacts with other experts in the company and in the field.

A collection of a hundred articles and preprints previously assembled by the NAPCA Project Officer was then melded into the file, to provide working copies and additional references not already at hand. A computer-based search programmed to highlight U.S. patents on NO_x removal and control processes was obtained from IFI-Plenum. This provided another hundred references selected from the 2194 patents issued from 1950 through 1966 which mention NO_x and a complete title, number, and partial key-word analysis for all patents in the list.

This complete patent reference list was subsequently rearranged into subject class order, according to the official classification schedule of the U.S. Patent Office. This makes it possible to locate quickly in any chemical subject class or sub-class, such as the manufacture of dibasic organic acids, all patents which mention nitrogen oxides or nitric acid. The key-number assigned by the computer searching also indicates at a glance which patents in each class deal with the concepts of removal, prevention, contamination or emission, which were highlighted in the original selection.

The IFI patent search is a convenient research tool, providing access to a large body of process information on NO_x emissions which is not available elsewhere in the literature. Transcripts of this search in its original form and in patent class order will be transmitted to NAPCA for possible use by APTIC in further searching.

The next step in augmenting the search was to analyze and classify the 400 entries in a NAPCA card file of transcripts from Chemical Abstracts, from 1956 through 1966, kindly transmitted to us by the Project Officer. This included material on NO_x reaction kinetics and mathematical modeling, which helped round out the picture of those portions of the literature where pertinent information is to be found. Coverage was extended in

Chemical Abstracts on this basis through 1967 and 1968, by a complete paging of sections deemed most pertinent to the project. Corresponding entries were covered in the Engineering Arts Index back to 1950, and in the cumulative indexes of Chemical Abstracts from 1956 through 1966 for all entries relating to the chemistry of NO_x emissions.

The basis of selecting pertinent references was continually refined during the search by the team evaluation of material at hand. Copies of some 500 original references were provided to the team members for this purpose. A final check of Chemical Abstracts from 1956 back to 1907 and a third run-through for the period 1956 to date added pertinent references indexed under flames and combustion to the list of areas searched. This search was completed for 1907 through 1968.

Special literature sources for pertinent material were also covered at the same time, such as the Penn State "Air Pollution Titles" starting in 1965 and the API "Subject Index to Current Literature on Air and Water Conservation" starting in 1967. Three visits to the Air Pollution Technical Information Center (APTIC) at Arlington provided references from their Termatrex index system on special topics. Numerous specialized indexes and proprietary information reviews were also consulted in our library, including previous Company reviews, Predicasts, SEARCH, and the Stanford Research Institute's Chemical Economics Handbook and Process Economics Reports which are not available for general circulation.

The searching strategy provided a continuous feedback of significant new references into the system, by the team members' selection of items from the bibliographies of the better references. Searching was continued until the percentage of "new" references from this or other sources found to be already in the file was well over 80% in most areas.

The literature in 1969 was covered broadly through Chemical Abstracts, the APTIC accessions list, the Engineering Arts Index and API bulletins, and more specifically by bibliography requests from team members based on their attendances at current technical meetings, preprints, and further study of older references. Significant references located through this search were supplied through NAPCA to the Air Pollution Technical Information Center, for incorporation into APTIC files.

The abstract card file was duplicated for convenience in three Xerox copies. The master file was kept in alphabetical order by author and used as the index for accession of original articles or Xerox copies, for distribution to individual team members. A duplicate author index was kept as a working file, and each team member received a working file of cards for his specific area. The fourth set was a working file for reclassification for keywords-by-process. The primary object of this reworking was to pick up new concepts or viewpoints to be considered in the further evaluation of the material at hand.

The bibliography attached to this report is a representative selection of about 25% of the references considered, and the complete card file is available. The references cited within each section are numbered in the order in which they appear in the text, and entered at the end of the section. The references cited plus selected supplementary references dealing with the same area are also combined in the bibliography at the end of the report, in alphabetical order by first author, for convenient use. An asterisk is set in the margin in this bibliography against each reference cited in the text.

A brief statistical analysis of the NO_x literature in the bibliography shows several trends based on the year of publication of the selected references. The problem of NO_x removal from stack gases has been important for the longest period of time, with half of the references cited from 1960 or before. The rate of publication has increased more rapidly in recent years in the areas of NO_x statistics, kinetics, and combustion modifications, particularly since 1965. The number of references cited per year in these areas has increased ten-fold between 1960 and 1968. References cited in the older art of NO_x removal have only doubled in the same time, in spite of the very rapid increase in interest in the NO_x field as a whole. In other words, most of which is new in the NO_x literature in recent years has dealt with aspects other than the removal of NO_x once formed.

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13. APPENDIX*

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* The first digits of the Appendices represent the section of this report to which they relate.

APPENDIX 3-1

STEAM-ELECTRIC PLANT SURVEY FOR CALENDAR YEAR 1967

ESSO RESEARCH AND ENGINEERING COMPANY
U.S. DEPARTMENT OF HEW, NATIONAL AIR POLLUTION CONTROL ADMINISTRATION CONTRACT (NUMBER PH-22-68-55)
"SYSTEMS STUDY OF NITROGEN OXIDE CONTROL METHODS FOR STATIONARY SOURCES"

Firm Name ________________ Mailing Address ________________

Plant Name and Location ________________ ________________

____

Person to Contact Re This Report ________ Title ________ Phone No. ________

SECTION I - BOILER INFORMATION.(1) Complete for each boiler or group of identical boilers (if necessary attach additional sheets).

1. Boiler Number or Numbers					1.
2. Steam Press, P.S.I.					2.
3. Maximum Con't Rating (MCR), 1000 lb. stm./hr.					3.
4. Initial Year of Operation					4.
5. Manufacturer					5.
6. Steam Temp., °F - Superheater/Reheater	/	/	/	/	6.
7. Design - Suction or Pressurized Furnace	S P	S P	S P	S P	7.
8. - Wet or Dry Bottom	W D	W D	W D	W D	8.
9. - Furnace Volume, Cubic Feet					9.
10. - Furnace Heating Surface, Sq. Ft.					10.
11. Stack Number(2)					11.
12. Stack Height/Diameter at Top, Feet	/	/	/	/	12.
13. Type of Firing(3) V, T, FW, S, Cy, HO, Tu					13.
14. Mixed Fuel(4), CF, SF					14.
15. Oil: Steam or Mech Atomization(5)	St. Me.	St. Me.	St. Me.	St. Me.	15.
16. Oil Pressure, PSI - Max.					16.
17. Gas: Burner Design(5)					17.
18. Coal: Burner Design(5)					18.
19. Windbox Pressure Inches H_2O (Full Load)					19.
20. Flyash Reinjection(6)					20.
Steam Temperature Control:					
21. - Attemperation(6)					21.
22. - Flue Gas Recirc., % Max.- Before/After Burner	B A	B A	B A	B A	22.
23. - Tilting Burners(6)					23.
24. Two-Stage Combustion(6) (See Section II)					24.
25. Boiler Efficiency-% (Full Load) Coal/Oil/Gas	/ /	/ /	/ /	/ /	25.

- - - - - - -

(1) Please attach boiler outline sketch similar to attachments.

(2) Give plant stack designation and height of stack into which boiler discharges.

(3) Vertical, Tangential, Front-Wall, Stoker, Cyclone, Horizontally Opposed, Turbo Furnace.

(4) Combination Firing (Alternate Burners on Different Fuels), Simultaneous Firing (2 Fuels in Same Burner/s).

(5) See attached sketches. Indicate burner configuration similar to Sketch A, B, C. If different, indicate type and manufacturer.

(6) (Yes or No).

APPENDIX 3-1 (CONT'D.)

FUEL DATA(7), Tons/Hr., bbl/hr., 1000 CF/hr.	Coal	Oil	Gas	Coal	Oil	Gas	Coal	Oil	Gas	Coal	Oil	Gas	
6. Max. Con't Rating (Full Load)													26.
7. 3/4 Load													27.
8. 1/2 Load													28.
9. Annual Consumption (1967) 1000 Tons, 1000 bbls., or 10^6 cu. ft.													29.
0. Av. Heat Content, BTU/lb., gal. or CF (Dry)													30.
1. Sulfur Content - Weight %(8)													31.
OPERATING DATA													
2. Flue Gas Rate - Full Load, 1000 lbs./hr.													32.
3. " " " - 3/4 Load " " "													33.
4. " " " - 1/2 Load " " "													34.
5. Excess Air/O_2,% - Full Load	/	/	/	/	/	/	/	/	/	/	/	/	35.
6. " " " - 3/4 Load	/	/	/	/	/	/	/	/	/	/	/	/	36.
7. " " " - 1/2 Load	/	/	/	/	/	/	/	/	/	/	/	/	37.
8. NO_x Emissions, ppm(9) (Calc. to 3% O_2) - Full Ld.													38.
9. " " " " " " " - 3/4 Ld.													39.
0. " " " " " " " - 1/2 Ld.													40.
1. No. of Burners - Full Load													41.
2. " " " - 3/4 Load													42.
3. " " " - 1/2 Load													43.
4. Preheated Air Temp. °F													44.
5. Burner Flame " "													45.
6. Flue Gas Entering Superheater " "													46.
7. Flue Gas Entering Economizer " "													47.
8. Flue Gas Entering Air Preheater " "													48.
9. Flue Gas Leaving Air Preheater " "													49.
0. Oil Atomizing Temperature °F													50.
1. Flue Gas Cleaning Equip.,(10) E,WS,Mech,Bag													51.
2. Efficiency of Gas Cleaning Equipment- %													52.

LOAD VARIATION (Number of Boiler Hours in Typical Week)	Summer	Winter	Summer	Winter	Summer	Winter	Summer	Winter	
3. No Load									53.
4. Less Than 40% Load									54.
5. 40-59% Load									55.
6 60-79% Load									56.
7. 80-99% Load									57.
8. Full Load									58.

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7) Assume single fuel firing.

8) Please attach typical analysis of fuel (ultimate preferred), ash and flyash. Also include % of ash collected as flyash, % ash collected as bottom ash. If analysis data not readily available, please give name and address of supplier.

(9) Complete only if data are available from stack tests (also state method used for NO_x analysis).

0) Electrostatic Precipitator, Wet Scrubber, Mechanical, Bag Filter.

APPENDIX 3-1 (CONT'D.)

SECTION II - TWO STAGE COMBUSTION INFORMATION SHEET

1. Boiler Number or Numbers				
2. Installed: A As Original Equipment or B Addition	A____ B____	A____ B____	A____ B____	A____ B____
3. Incremental Installation Cost, 1000$				
4. Reduction in Boiler Efficiency (If Any), %				
5. Increased Maintenance Cost (If Any), $ Per Year				
6. Incremental Operating Costs,* Mils Per 1000 lbs. of Steam				
7. Reduction in NO_x Emissions at Full Load, %				
8. Other Benefits:				
9. % Stoichiometric Air: A 1st Stage, B 2nd Stage Ports	A____ B____	A____ B____	A____ B____	A____ B____

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* If Available.

APPENDIX 3-1 (CONT'D.)

Plant Name ____________________ Location ____________________

SECTION III - PEAK SHAVING UNITS (Gas Turbines - Internal Combustion Engines)

1. Unit Number(s) (Group Identical Units)					1.
2. Nameplate Rating, KW					2.
3. Year Installed					3.
4. Manufacturer					4.
5. Manufacturers Model No.					5.
6. If Diesel: A, B, C, D, E (1)					6.
7. If Gas Turbine: A) Aircraft Type, B) Industrial Type					7.
8. Fuel Consumption, BTU/KW @ Full Load					8.
9. Kind of Fuel (Nat. Gas, Kerosene, Diesel Fuel, Etc.)					9.
10. Fuel Oil Analysis: (2) - Gravity, °API					10.
- Viscosity, SSU/100°F (or other)					
- Hydrogen % (if Available)					
- Sulfur, Ash (Wt. %)	S A	S A	S A	S A	
- Vanadium, Sodium (PPM)	V S	V S	V S	V S	
11. Average Heat Content of Fuel, BTU/lb., Gal., or Cu. Ft.					11.
12. Annual Fuel Consumption - 1967, Bbls, 1000's Cubic Ft.					12.
13. Operating Hours Per Year					13.
14. Exhaust Gas Temp, °F					14.
15. Inlet Gas Temp., °F (3)					15.
16. Fuel Air Ratio, lb. Fuel/lb. Air (3)					16.
17. Pressure Ratio (Compression) (3)					17.
18. Nitrogen Oxide Emission at Full Load, lb./Hour (4)					18.
19. Height of Stack, Ft.					19.

---

(1) A 2-Cycle, Air Scavenged; B 4-Cycle Turbocharged; C 2-Cycle Normally Aspirated (NA) Low Speed (about 300 RPM); D 4-Cycle (NA) Medium Speed (about 1800 RPM); E 4-Cycle (NA) High Speed (about 3200 RPM).

(2) If not available, give name and address of fuel supplier.

(3) Applies primarily to gas turbine - available from manufacturer's catalog, etc.

(4) Fill in if measured by actual test and designate test method used.

APPENDIX 3-2

STEAM-ELECTRIC PLANT SURVEY INSTRUCTIONS

SECTION I - BOILER INFORMATION

Although most of this questionnaire is self-explanatory, the following instructions are given to clarify and simplify specific lines. This form provides 4 columns for information on boilers. Information on boilers which are physically identical may be grouped into a single column. However, boilers of different size, type of firing, etc., should be listed in separate columns. (Please note example survey form.) Where an item is not applicable in a specific instance, insert N.A. rather than leaving the item blank.

Line 1 - Boiler Number or Numbers - Give the number of physically identical boilers.

Line 3 - Maximum Continuous Rating - Give either manufacturer's rating or sustained operating capability. However, it is important that Fuel Data on lines 26 through 29 are consistent with line 3 data.

Lines 9 and 10 - Furnace Volume and Heating Surface - From manufacturer's performance sheet.

Line 14 - Mixed Fuels - If two fuels are burned simultaneously in a single burner indicate SF, Simultaneous Firing (two fuels in same burner). Indicate CF, Combination Firing, for two fuels burned simultaneously in separate burners.

Lines 15, 17 and 18 - See attached sketches. Indicate burner configuration similar to Sketch A, B, C. If different, indicate type and manufacturer.

Line 24 - If answer is yes, please complete Section II Two Stage Combustion Information Sheet.

Lines 26-8 - Fuel Data - Give fuel consumption assuming only one fuel burned at a time (no mixed or simultaneous firing).

Line 32 - Flue Gas Rate - CF/M from manufacturer's performance sheet.

Lines 35-37 - Please give % excess air or O_2 in flue gas, depending upon whichever is available.

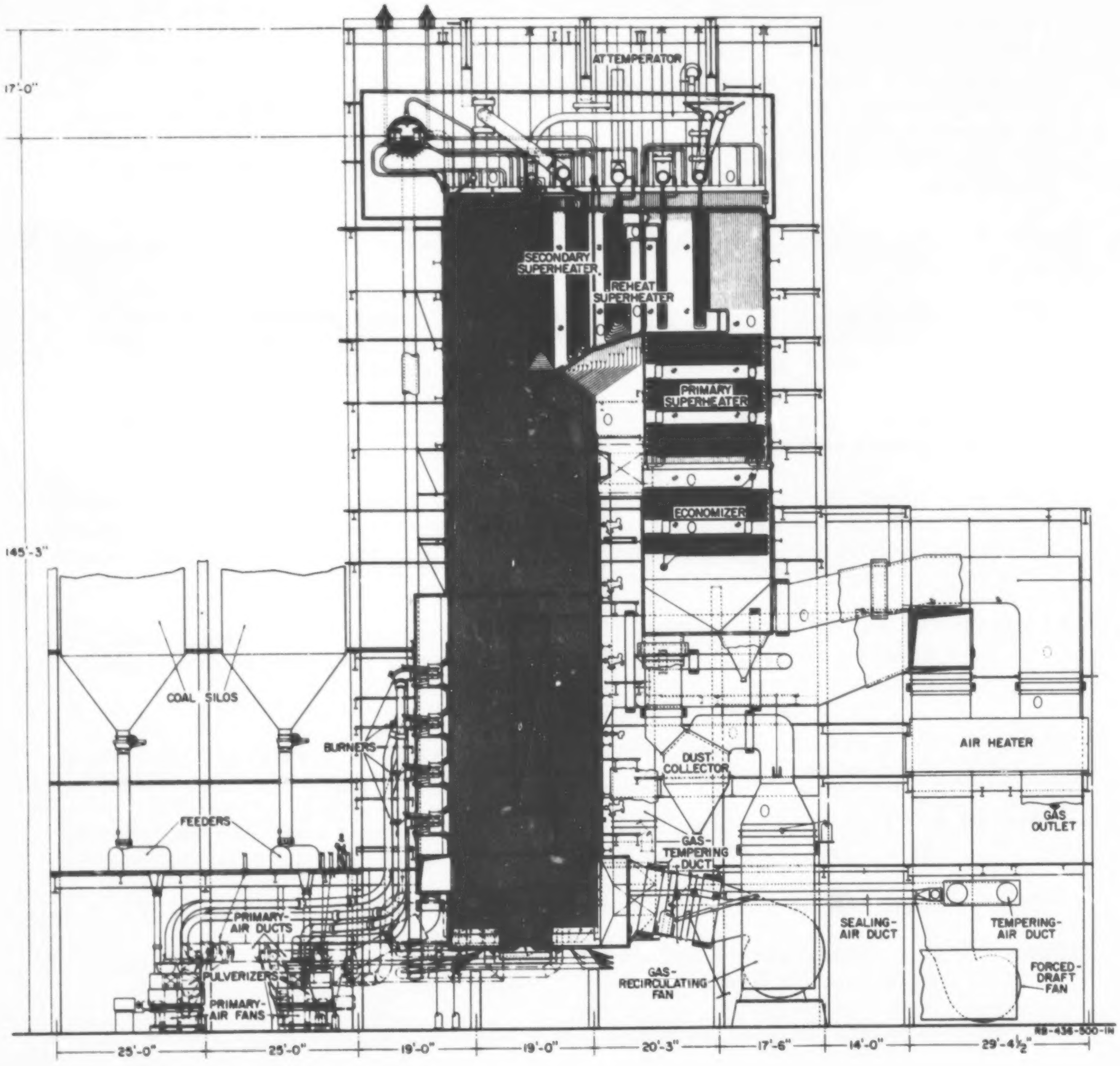
Line 45 - Complete only if data are available from measurements.

Line 46 - Generally available from manufacturer's performance sheet.

Lines 49-54 - Load Variation - Please estimate number of boiler-hours in typical week of summer and winter within each specified load range. Where a single column represents data from a number of identical boilers, report combined boiler-hours in each load range. See example survey form where the first column covers the identical boilers.

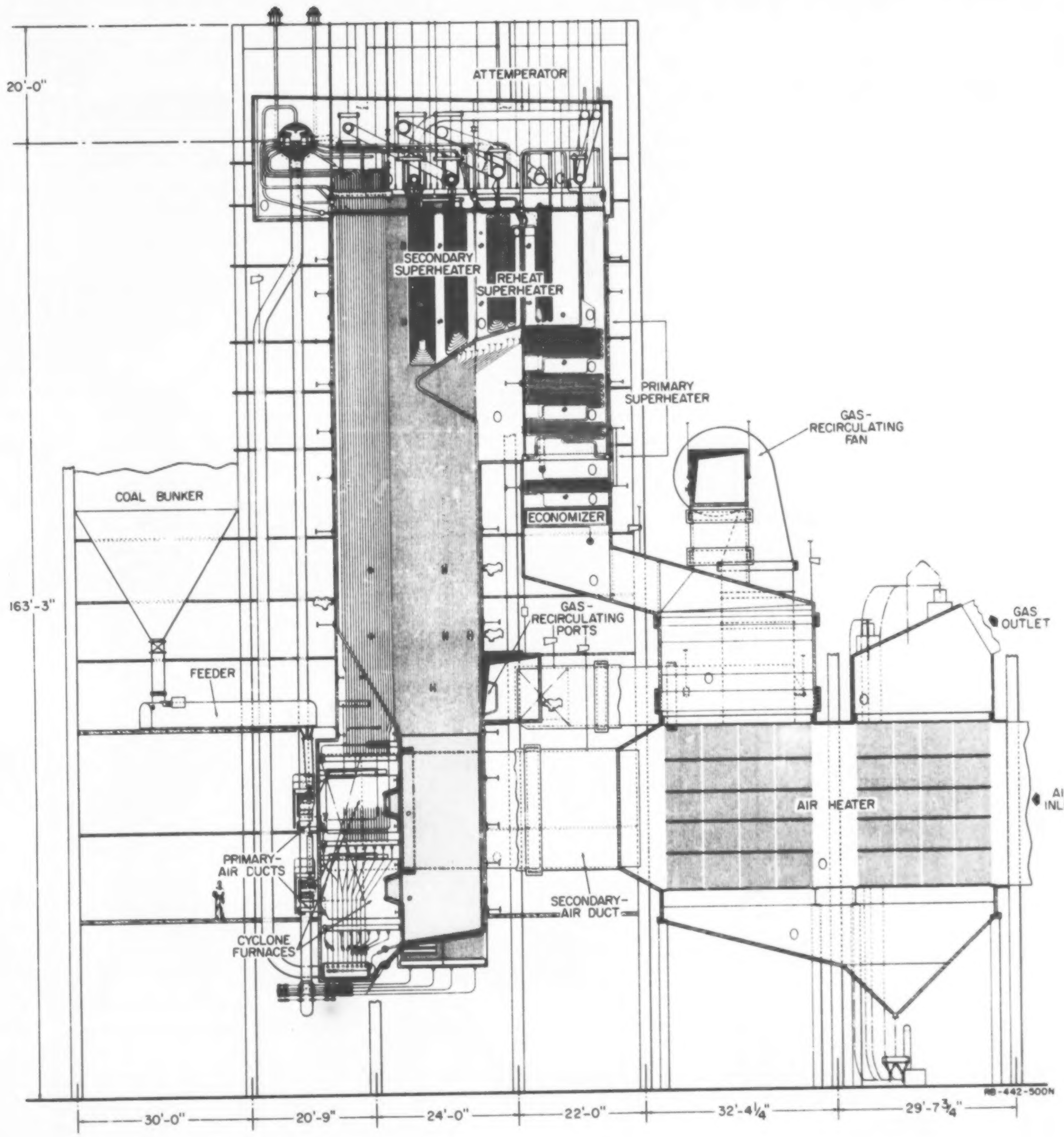
APPENDIX 3-2 (CONT'D.)

TYPICAL BOILER OUTLINE SKETCH


ATTEMPERATOR
17'-0"
SECONDARY SUPERHEATER
REHEAT SUPERHEATER
PRIMARY SUPERHEATER
ECONOMIZER
145'-3"
COAL SILOS
BURNERS
DUST COLLECTOR
AIR HEATER
GAS OUTLET
FEEDERS
GAS-TEMPERING DUCT
SEALING-AIR DUCT
TEMPERING-AIR DUCT
PRIMARY-AIR DUCTS
PULVERIZERS
PRIMARY-AIR FANS
GAS-RECIRCULATING FAN
FORCED-DRAFT FAN
RB-436-500-IN
25'-0"
25'-0"
19'-0"
19'-0"
20'-3"
17'-6"
14'-0"
29'-4½"

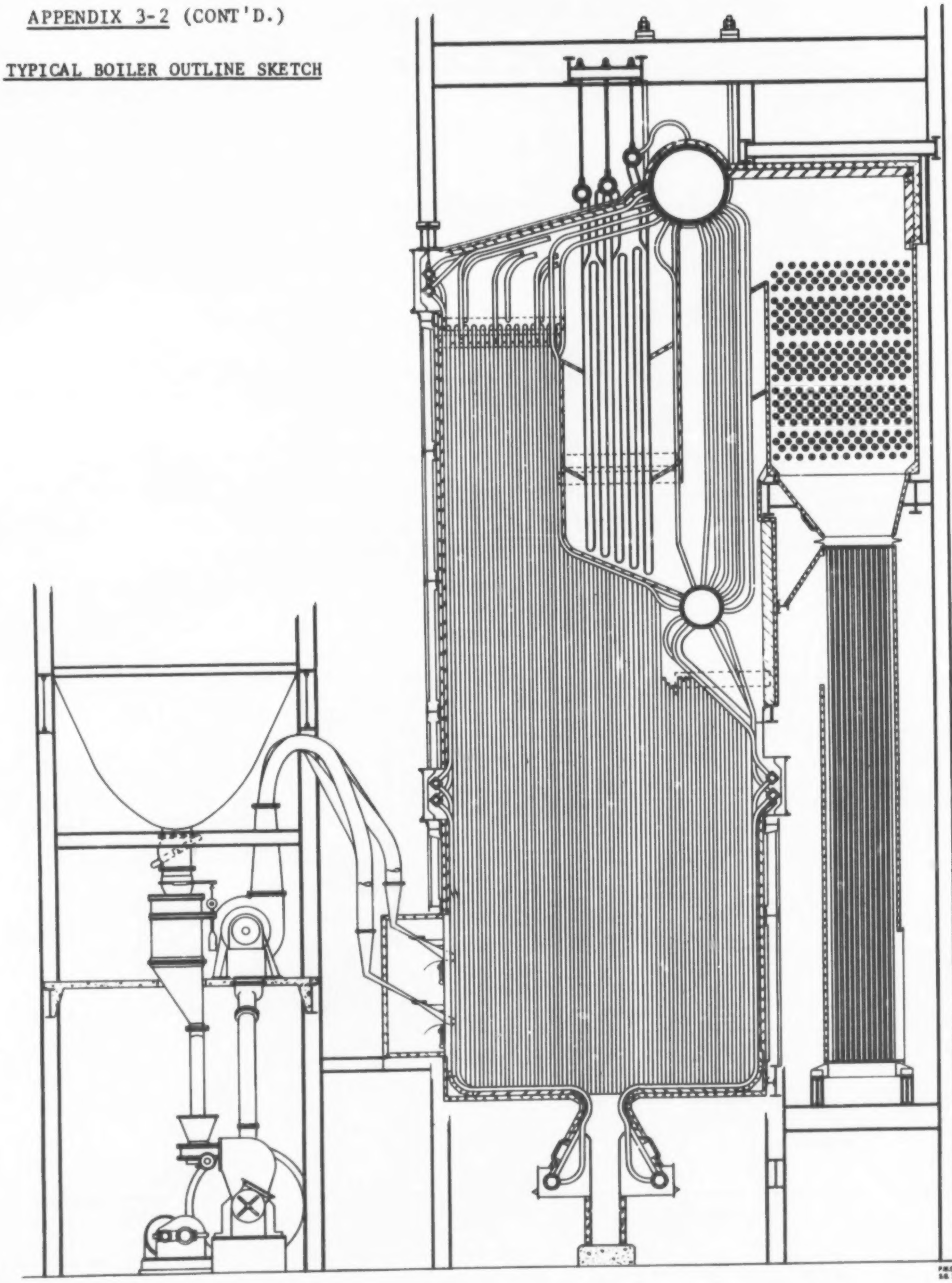
APPENDIX 3-2 (CONT'D.)

TYPICAL BOILER OUTLINE SKETCH


20'-0"
ATTEMPERATOR
SECONDARY SUPERHEATER
REHEAT SUPERHEATER
PRIMARY SUPERHEATER
GAS-RECIRCULATING FAN
COAL BUNKER
ECONOMIZER
163'-3"
GAS-RECIRCULATING PORTS
GAS OUTLET
FEEDER
AIR HEATER
AIR INLET
PRIMARY-AIR DUCTS
SECONDARY-AIR DUCT
CYCLONE FURNACES
RB-442-500N
30'-0"
20'-9"
24'-0"
22'-0"
32'-4¼"
29'-7¾"

APPENDIX 3-2 (CONT'D.)

TYPICAL BOILER OUTLINE SKETCH

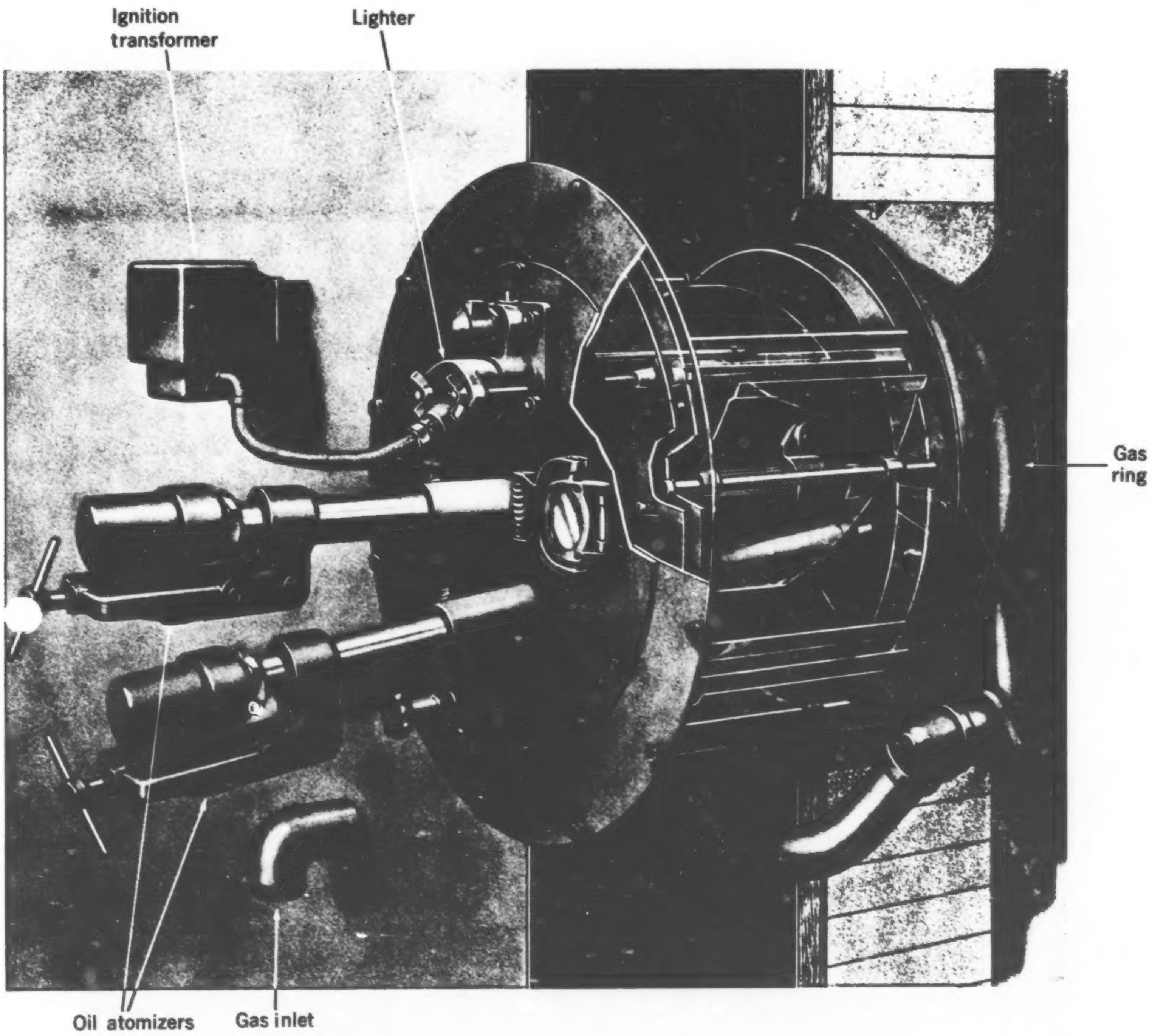


APPENDIX 3-2 (CONT'D.)

SKETCH A

GAS - RING TYPE BURNER

BDS
410
924Z
12-66

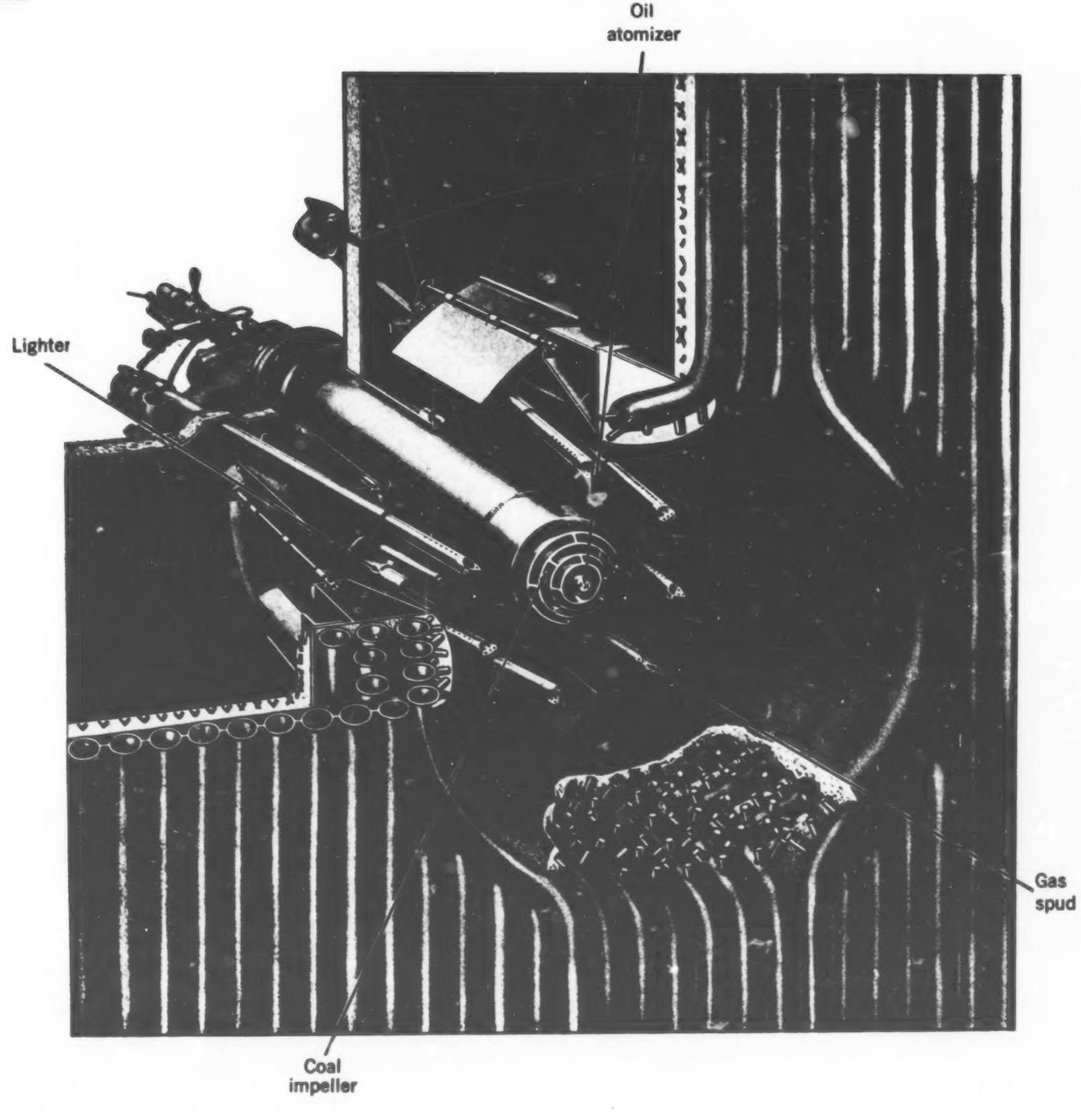

Ignition transformer
Lighter
Gas ring
Oil atomizers
Gas inlet

APPENDIX 3-2 (CONT'D.)

SKETCH B

GAS - SPUD TYPE
OIL - CIRCULAR REGISTER
COAL - CIRCULAR REGISTER

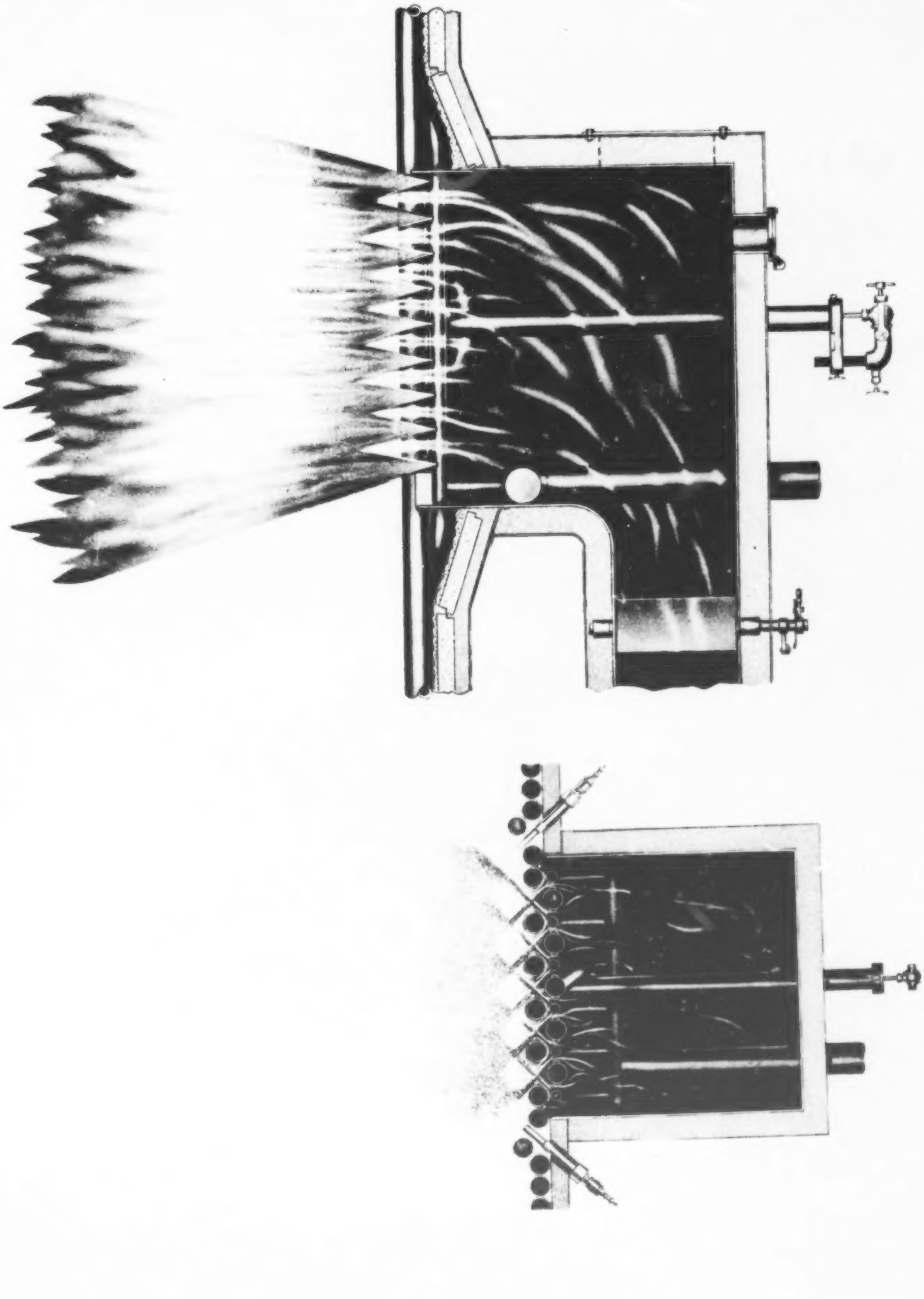
BDS
410
104LRZ
10-68


Oil
atomizer
Lighter
Gas
spud
Coal
impeller

APPENDIX 3-2 (CONT'D.)

SKETCH C

INTERTUBE TYPE - SHOWN FOR GAS AND OIL, SIMILAR FOR PULVERIZED COAL



APPENDIX 3-3

STEAM-ELECTRIC PLANT SURVEY FOR CALENDAR YEAR 1967

ESSO RESEARCH AND ENGINEERING COMPANY
U.S. DEPARTMENT OF HEW, NATIONAL AIR POLLUTION CONTROL ADMINISTRATION CONTRACT (NUMBER PH-22-68-55)
"SYSTEMS STUDY OF NITROGEN OXIDE CONTROL METHODS FOR STATIONARY SOURCES"

Firm Name XYZ Electric Company

Plant Name and Location New York
New York

Mailing Address 1284 Rahway Avenue
Westfield, New Jersey 07090

Person to Contact Re This Report John Doe

Title Chief Mech. Eng.

Phone No. 201-474-3128

SECTION I - BOILER INFORMATION.[1] Complete for each boiler or group of identical boilers (if necessary attach additional sheets).

1.	Boiler Number or Numbers	3 Boilers	1			1.
2.	Steam Press, P.S.I.	2400	1050			2.
3.	Maximum Con't Rating (MCR), 1000 lb. stm./hr.	1000	675			3.
4.	Initial Year of Operation	1957, 1958, 1958	1949			4.
5.	Manufacturer	B&W	C. E.			5.
6.	Steam Temp., °F - Superheater/Reheater	1050 /1000	905 /	/	/	6.
7.	Design - Suction or Pressurized Furnace	S P X	S X P	S P	S P	7.
8.	- Wet or Dry Bottom	W D X	W D X	W D	W D	8.
9.	- Furnace Volume, Cubic Feet	66,200	44,800			9.
10.	- Furnace Heating Surface, Sq. Ft.	16,000	10,800			10.
11.	Stack Number[2]	S-1, S-2, S-2	S-4			11.
12.	Stack Height/Diameter at Top, Feet	300,500,500 /20,25,25	300 / 22	/	/	12.
13.	Type of Firing[3] V,T,FW,S,Cy,HO,Tu	FW	T			13.
14.	Mixed Fuel(4), CF, SF	N.A.	N.A.			14.
15.	Oil: Steam or Mech Atomization(5)	St. Me. B	St. N.A. Me. N.A.	St. Me.	St. Me.	15.
16.	Oil Pressure, PSI - Max.	1000	N.A.			16.
17.	Gas: Burner Design(5)	N.A.	B			17.
18.	Coal: Burner Design(5)	N.A.	B			18.
19.	Windbox Pressure Inches H_2O (Full Load)	25	6.61			19.
20.	Flyash Reinjection(6)	No	No			20.
	Steam Temperature Control:					
21.	- Attemperation(6)	Yes	No			21.
22.	- Flue Gas Recirc., % Max.- Before/After Burner	B 0 A 7.5%	B 0 A 0	B A	B A	22.
23.	- Tilting Burners(6)	No	Yes			23.
24.	Two-Stage Combustion(6) (See Section II)	No	No			24.
25.	Boiler Efficiency-%(Full Load) Coal/Oil/Gas	-- / 88.5 / --	85.5/ -- / 81.0	/ /	/ /	25.

- - - - - - -

(1) Please attach boiler outline sketch similar to attachments.

(2) Give plant stack designation and height of stack into which boiler discharges.

(3) Vertical, Tangential, Front-Wall, Stoker, Cyclone, Horizontally Opposed, Turbo Furnace.

(4) Combination Firing (Alternate Burners on Different Fuels), Simultaneous Firing (2 Fuels in Same Burner/s).

(5) See attached sketches. Indicate burner configuration similar to Sketch A, B, C. If different, indicate type and manufacturer.

(6) (Yes or No).

APPENDIX 3-3 (CONT'D.)

	FUEL DATA(7), Tons/Hr., bbl/hr., 1000 CF/hr.	Coal	Oil	Gas	Coal	Oil	Gas	Coal	Oil	Gas	Coal	Oil	Gas	
26.	Max. Con't Rating (Full Load)		182		32.8		938							26.
27.	3/4 Load		137		24.9		712							27.
28.	1/2 Load		92		17.0		487							28.
29.	Annual Consumption (1967) 1000 Tons, 1000 bbls., or 10^6 cu. ft.		960		54		1158							29.
30.	Av. Heat Content, BTU/lb., gal. or CF (Dry)		18,300		13,500		1010							30.
31.	Sulfur Content - Weight %(8)		2.2		1.6		0							31.
	OPERATING DATA													
32.	Flue Gas Rate - Full Load, 1000 lbs./hr.		1,370		910		920							32.
33.	" " " - 3/4 Load " " "		1,040		692		704							33.
34.	" " " - 1/2 Load " " "		720		473		480							34.
35.	Excess Air/O_2,% - Full Load	/	/2.0	/	20/	/	15/	/	/	/	/	/	/	35.
36.	" " " - 3/4 Load	/	/2.5	/	22/	/	16/	/	/	/	/	/	/	36.
37.	" " " - 1/2 Load	/	/3.0	/	24/	/	18/	/	/	/	/	/	/	37.
38.	NO_x Emissions, ppm(9) (Calc. to 3% O_2) - Full Ld.		750		850		700							38.
39.	" " " " " " " - 3/4 Ld.		600		640		585							39.
40.	" " " " " " " - 1/2 Ld.		480		500		430							40.
41.	No. of Burners - Full Load		12		8		8							41.
42.	" " " - 3/4 Load		12		8		8							42.
43.	" " " - 1/2 Load		6		4		4							43.
44.	Preheated Air Temp. °F		530		540		500							44.
45.	Burner Flame " "		2900		2750		2800							45.
46.	Flue Gas Entering Superheater " "		2150		2150		2200							46.
47.	Flue Gas Entering Economizer " "		975		1050		1075							47.
48.	Flue Gas Entering Air Preheater " "		730		750		760							48.
49.	Flue Gas Leaving Air Preheater " "		320		300		340							49.
50.	Oil Atomizing Temperature °F		220		N.A.		N.A.							50.
51.	Flue Gas Cleaning Equip.,(10) E,WS,Mech,Bag		N.A.		E		N.A.							51.
52.	Efficiency of Gas Cleaning Equipment - %		N.A.		97		N.A.							52.

	LOAD VARIATION (Number of Boiler Hours in Typical Week)	Summer	Winter	Summer	Winter	Summer	Winter	Summer	Winter	
53.	No Load	100	80	74	60					53.
54.	Less Than 40% Load									54.
55.	40-59% Load		20							55.
56.	60-79% Load	80	70							56.
57.	80-99% Load	40	60							57.
58.	Full Load	220	210	74	88					58.
	Total	444	444	148	148					

- - - - - - - - -

(7) Assume single fuel firing.

(8) Please attach typical analysis of fuel (ultimate preferred), ash and flyash. Also include % of ash collected as flyash, % ash collected as bottom ash. If analysis data not readily available, please give name and address of supplier.

(9) Complete only if data are available from stack tests (also state method used for NO_x analysis).

(10) Electrostatic Precipitator, Wet Scrubber, Mechanical, Bag Filter.

APPENDIX 3-4

Summary of Steam Electric Plant Survey for Calendar Year 1967

Appendix 3-4, Summary of Steam Electric Plant Survey for Calendar Year 1967 presents the number of boilers classified according to fuel burned, type of firing and steam rate (thousands of pounds per hour). It should be noted that boilers which burned sizable quantities of two fuels have been classified under each of the fuels burned; therefore, data on 480 boilers show up as 670 boilers when classified by fuel burned.

The bulk of boilers (87%) operated by 13 reporting companies are relatively small, i.e., less than 2 million pounds of steam per hour (or less than 280 Megawatt capacity). The average conventional steam boiler installed in 1969 had a steam rate of about 3.2 million pounds per hour.

The most common type of firing for coal burning boilers was tangential, while front wall firing was the most common design for both gas and oil fired units. However, the larger boilers installed in the last few years are horizontally opposed or tangential for gas and oil firing, and tangential or cyclone for coal fired units.

APPENDIX 3-4 (CONT'D.)

SUMMARY OF STEAM ELECTRIC PLANT SURVEY
(NUMBER OF BOILERS BY FUEL, TYPE OF FIRING AND STEAM RATE)

Maximum Continuous Rating (10^3 Lbs. Steam/Hr)	Fossil Fuel Burned																					Grand Total
	Coal								Gas						Oil							
	FW	HO	T	V	S	CY	O	TOT	FW	HO	T	CY	O	TOT	FW	HO	T	V	O	TOT		
0 to 1000	13		22	30	53	9	26	153	72		5	8	4	89	122	2	10	12	4	150		392
1000 to 2000	15		51			4	10	80	34	9	1	2	5	51	44	9	4		3	60		191
2000 to 3000	3		7			6	1	17	3	8	6	4		21	3	9	6		2	20		58
3000 to 4000		1	3					4		5	2			7		4	2			6		17
4000 to 5000						3		3														3
5000 to 6000										2				2		2				2		4
6000 and over			3					3									2			2		5
Total	31	1	86	30	53	22	37	260	109	24	14	14	9	170	169	26	24	12	9	240		670

Key:			
FW	Front Wall	S	Stoker
HO	Horizonally Opposed	CY	Cyclone
T	Tangential	O	Other
V	Vertical	TOT	Total

APPENDIX 3-5

SUMMARY OF STEAM-ELECTRIC PLANT SURVEY FOR CALENDAR YEAR 1967 - BOILER DESIGN AND OPERATING DATA

This table summarizes selected boiler design and operating information reported on the Steam-Electric Plant Survey for Calendar Year 1967 for boilers with measured NO_x emission rates. NO_x emission data were reported on 40 groups of boilers (92 individual boilers were evaluated in the 40 groups of physically similar boilers). Since 90% of this information was obtained from only three West Coast companies, it cannot be used to accurately represent United States steam-electric boilers or even the 13 companies which comprise a stratified sample of United States electric-power companies. However, the table is useful in illustrating the wide variety of boiler designs and operating conditions that must be considered in establishing NO_x emission factors.

NO_x emission rates (ppm at 3% oxygen in flue gas) varied from 400 to 1147 in coal-fired boilers (average of 774), from 47 to 902 in gas-fired boilers (average of 396), and from 110 to 800 in oil-fired boilers (average of 429). Variables that affect emission rates include boiler size (steam rate), type of firing, % excess air flue gas temperature entering superheater, flue gas recirculation, heat release rate and heat transfer rate. However, to develop meaningful, general quantitative relationships between design and operating data and NO_x emission rates will require considerably more data than those reported in this survey.

APPENDIX 3-1 (CONT'D.)

SUMMARY OF STEAM ELECTRIC PLANT SURVEY FOR CALENDAR YEAR 1967
BOILER INFORMATION AND NO_x EMISSION RATES

				Boiler Design Information												Operating and Emission Data								
																						Flue Gas Temp.		
No. of Boilers	Steam Rate at Max. Continuous Rating 10^3 Lb Steam/Hr	Initial Year of Operation(c)	Manufacturer	Suction or Pressure Furnace	Wet or Dry Bottom	Furnace Volume (10^3 Cubic Feet)	Furnace Heating Surface (10^3 Square Feet)	Stack Height (Feet)	Stack Diameter at Top (Feet)	Type of Firing	Windbox Pressure Inches H_2O @ Full Load	Attemperation	Maximum % Flue Gas Recirculation Before or After Burner	Coal, Oil, Gas Fuel	Fuel Burned/Hour at Max. Cont. Rating, Tons/Hr; Bbl/Hr; 10^3 Ft³/Hr	Fuel Consumption - 1967, 10^3 Tons 10^3 Bbl; 10^6 cu ft	Ave. Fuel Heat Content 10^2 Btu/Lb, Gal or 10^2 Ft³	Flue Gas Rate - Full Load 10^3 Lbs/Hr	% Excess Air @ Full Load	No. Burners at Full Load	Preheated Air Temperature - °F	Entering Superh	Leaving Air Preheater	NO_x Emissions at Full Load (ppm)(d)
1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25
6	600	1950 1951	B & W	S	(b)	31.9	6.5	225	11	FW	6	N	(a)	O G	100 600	553 100	153 109	652 646	15 10	9 9	596 621	(a) (a)	343 358	473 315
2	850	1952	B & W	S	(b)	54.9	14.1	225	13	FW	12	Y	26B	O G	200 1,200	402 79	153 109	1,110 1,100	15 10	12 12	600 610	(a (a	321 340	550 377
2	5,300	1967 1968	B & W	P	(b)	230	30.8	500	20	HO	22	Y	14B	O G	1,000 6,000	(a) 20	153 109	5,558 5,364	10 5	48 40	575 554	(a (a	252 249	313 146
6	550	1951	C.E.	S	(b)	34.7	23.8	200	11	FW	6	N	(a)	O G	101 648	6 12	153 106	685 678	18 13	9 9	530 594	2,010 2,045	353 369	320 47
2	850	1953	C.E.	S	(b)	50	29.2	200	16	FW	10	Y	(a)	O G	183 1,172	22 19	153 106	1,144 1,120	18 15	12 12	483 496	2,040 2,140	329 347	585 108
2	2,000	1964	B & W	P	(b)	84.5	15.4	450	22	HO	19	Y	30A	O G	491 3,144	96 135	153 106	2,830 2,846	12 9	24 24	586 610	2,460 2,600	289 269	296 460
1	498	1956	B & W	S	(b)	16.2	25.7	120	10	FW	6	Y	(a)	O G	96 641	2 13	152 101	559 580	10 10	6 6	530 532	2,190 (a)	330 346	220 276
1	498	1958	R	P	(b)	19.6	15.4	120	10	FW	13	Y	(a)	O G	98 653	2 13	152 101	586 607	10 10	6 6	588 620	2,145 2,320	341 339	347 277
[illegible]	1,280	1955	B & W	S	D	90.7	19.4	300	17	FW	1	Y	0	C	76	1,856	12.5	1,744	20	18	591	(a)	305	400
2	4,900	1963	B & W	P	W	361	41.1	600	28	CY	43	Y	30A	C	308	4,074	11.7	3,820	20	14	595	2,245	290	1,147
3	1,000	1957	B & W	P	(b)	44.8	12.7	226	12	FW	20	Y	0	O	200	[illegible]	146	1,005	5	12	566	2,000	252	800
1	1,900	1957	B & W	P	(b)	92.0	30.9	226	12	FW	20	Y	0	O	425	2,800	146	2,106	8	24	570	2,000	276	800
4	317	1948 1949	B & W	S	(b)	20.6	4.8	200	13	FW	11	Y	0B 0A	O G	96 602	80 2,189	153 108	653 663	14 11	6 6	580 630	(a) (a)	419 445	481 524
1	1,170	1958	C.E.	S	(b)	90.4	22.1	250	[illegible]	FW	7	Y	0B 23A	O G	242 1,522	113 10,075	153 108	1,364 1,535	11 8	15 15	517 530	2,10[illegible] 2,143	303 303	390 383
2	1,170	1955 1956	C.E.	S	(b)	90.4	22.1	450	15	HO	9	Y	20B 0A	O G	250 1,528	260 8,739	18 108	1,664 1,546	15 10	15 15	517 515	2,1[illegible] 2,1[illegible]	331 327	381 228
2	2,160	1962 1963	B & W	P	(b)	84.5	45.5	450	18	HO	16	Y	0B 0A	O G	479 2,928	604 21,364	17.9 100	2,825 2,819	14 10	24 24	582 560	(a) (a)	259 253	335 444
4	1,800	1954	B & W	S	(b)	78.5	12.9	212	11	FW	12.5	Y	0B 50A	O G	249 1,573	89 3,841	152 107	1,550 1,530	15 11	16 16	625 625	2,080 2,130	265 276	437 457
2	2,400	1960 1961	B & W	P	(b)	133.5	24.9	450	14	HO	18	Y	0B 0A	O G	455 2,876	285 14,243	152 107	2,770 2,722	11 6	24 24	581 597	2,4[illegible]0 2,6[illegible]0	265 238	358 902
2	450	1931	B & W	S	(b)	15.1	12.3	11	24	FW	4	Y	(b)	O G	76.4 476	18 2,660	153 106	585 585	15 10	26 26	380 396	(a) (a	330 325	286 250
1	500	1931	B & W	S	(b)	15.1	12.3	11	24	FW	4	N	(b)	O G	76.4 746	(a)	153 106	507 507	15 10	22 22	380 340	(a) (a)	320 [illegible]	286 250
1	1,505	1965	R	P	(b)	76.3	10.3	30	11	HO	12.5	Y	(b)	O G	296 1,846	174 9,113	153 106	1,784 1,784	13 8	14 14	665 665	2,030 2,1[illegible]0	265 250	310 238

(a) Data not reported.
(b) Not applicable.
(c) Initial year of operation for 2 or more boilers indicate the earliest and latest initial year among the group of boilers.
(d) ppm corrected to 3% oxygen in the flue gas.

Codes: Column 4 - B & W - Babcock and Wilcox
C.E. - Combustion Engineering
R - Riley

Column 11 - FW, Frontwall; HO, Horizontally Opposed; CY, Cyclone; T, Tangential; AW, All Wall Fired.

Column 13 - Y, Yes; N, No

APPENDIX 3-5 (CONT'D.)

SUMMARY OF STEAM ELECTRIC PLANT SURVEY FOR CALENDAR YEAR 1967
BOILER INFORMATION AND NO_x EMISSION RATES

				Boiler Design Information											Operating and Emission Data									
No. of Boilers	Steam Rate at Max. Continuous Rating 10^3 Lb Steam/Hr	Initial Year of Operation(c)	Manufacturer	Suction or Pressure Furnace	Wet or Dry Bottom	Furnace Volume (10^3 Cubic Feet)	Furnace Heating Surface (10^3 Square Feet)	Stack Height (Feet)	Stack Diameter at Top (Feet)	Type of Firing	Windbox Pressure Inches H_2O @ Full Load	Attemperation	Maximum % Flue Gas Recirculation Before or After Burner	Coal, Oil, Gas Fuel	Fuel Burned/Hour at Max. Cont. Rating, Tons/Hr; Bbl/Hr; 10^3 Ft^3/Hr	Fuel Consumption - 1967, 10^3 Tons; 10^3 Bbl; 10^8 cu ft	Ave. Fuel Heat Content 10^3 Btu/Lb. Gal or 10^2 Ft^3	Flue Gas Rate - Full Load 10^3 Lbs Hr	% Excess Air @ Full Load	No. Burners at Full Load	Preheated Air Temperature - °F	Flue Gas Temp. Entering Superh	Flue Gas Temp. Leaving Air Preheater	NO_x Emissions at Full Load (ppm)(d)
1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25
2	1,510	1962 1963	C.E.	P	(b)	92.5	21.0	240	18	FW	17	Y	(b)B OA	O G	328 2,150	500 7,870	151 107	1,750 1,950	9 7	12 12	635 645	1,960 1,960	260 265	495 230
2	1,575	1964 1965	B & W	P	(b)	71.9	29.8	240	14	HO	24	Y	(b) (b)	O G	338 2,150	500 7,870	151 107	1,870 1,825	13 7	12 12	585 585	2,280 2,280	259 250	405 144
2	2,060	1966 1967	B & W	P	(b)	109.9	15.9	240	21	HO	(B)	Y	20B (b)A	O G	450 2,600	500 10,490	151 107	2,770 2,890	9 7	24 24	568 568	2,650 2,650	251 251	442 700
2	850	1954	B & W	P	(b)	49.0	12.4	250	2.5	FW	7.0	Y	(b)B 40A	O G	172 960	150 2,920	151 105	1,020 1,005	10 7	12 12	575 575	1,980 1,980	340 340	550 145
2	1,200	1955 1956	R	P S	(b)	88.4	18.4	250	15	FW	6.6	Y	(b)B (b)A	O G	282 1,620	175 6,914	151 105	1,644 1,620	12 9	20 20	593 593	1,915 1,915	302 302	(a) 178
2	1,200	1958 1959	C.E.	P S	(b)	65.0	20.4	300	20	FW	5.7	Y	(b)	O G	260 1,550	325 7,670	151 107	1,680 1,880	15 6	16 16	550 550	2,105 2,105	300 300	600 405
2	700	1943 1947	R	P	(b)	22.5	6.8	250	12	FW	6.0	Y	(b)B (a)A	O G	150 810	50 0.65	151 107	820 820	12 7	10 10	470 (B)	1,800 1,700	310 310	570 (a)
3	810	1948 1949	R	P	(b)	31.8	8.5	250	12	FW	6.0	Y	(b)B (a)A	O G	177 1,000	50 1.7	151 107	820 820	12 7	12 12	(B) (B)	2,040 2,090	275 270	525 270
2	920	1953	C.E.	P	(b)	50.4	33.5	(a)	(a)	T	(a)	Y	OB (a)A	O G	(a) (a)	1,665 35,416	18.5 103	(a) (a)	(a) (a)	(a) (a)	528 551	(a) (a)	278 307	190 135
2	2,305	1963	C.E.	P	(b)	112.5	(a)	200	0.5	T	22	Y	(a)B OA	O G	154 2,650	(a) (a)	18.0 107	2,445 2,460	10 8	24 24	638 625	2,150 2,310	258 244	300 300
2	1,140	1955	B & W	P	(b)	83.0	21.0	113	13	FW	6.9 7.2	Y	OB (a)A	O G	86 1,637	1,400 35,868	18.0 103	1,529 1,582	13 13	16 16	611 618	(a) (a)	274 281	580 450
2	2,260	1964	C.E.	P	(b)	112.0	(a)	113	13	T	22	Y	(a)B OA	O G	154 2,790	(a) (a)	18.0 107	2,445 2,460	10 8	24 24	638 642	2,150 2,310	257 249	300 300
2	1,254	1957	B & W	P	(b)	(a)	(a)	200	(a)	FW	7.9 8.4	Y	OB (a)A	O G	86.3 1,637	1,071 50,016	18.0 103	1,529 1,582	13 13	16 16	621 634	(a) (a)	283 296	580 450
2	3,316	1966	B & W	P	(b)	161.9	24.7	200	(a)	HO	3.9 4.3	Y	OB (a)A	O G	2,370 4,130	(a) (a)	18.0 109	3,820 3,825	10 10	16 16	562 545	(a) (a)	245 282	(a) 847
2	1,140	1957	B & W	P	(b)	83.0	21.0	109	12	FW	7.9	Y	OB (a)A	O G	86.3 (a)	2,807 66,216	18.0 (a)	1,529 (a)	13 (a)	16 (a)	627 (a)	(a) (a)	274 (a)	580 450
2	2,305	1962	C.E.	P	(b)	112.5	(a)	200	(a)	T	7.9	Y	(a)B OA	O G	154 2,650	(a) (a)	18.0 109	2,445 2,460	10 8	24 24	638 625	2,16[illegible] 2,31[illegible]	257 242	300 300
2	3,316	(a)	B & W	P	(b)	161.9	24.7	200	(a)	HO	4.0 4.3	Y	OB (a)A	O G	2,370 4,130	(a) (a)	18.0 109	3,820 3,825	10 10	16 16	562 545	(a) (a)	245 282	(a) 7[illegible]7
2	1,560	1958	B & W	P	(b)	91.9	(a)	203	17	FW	6.3 6.7	Y	OB (a)A	O G	116,880 36,000	829 31,523	18.0 103	1,957 1,986	7 8	24 24	601 611	2,37[illegible] 2,54[illegible]	278 293	440 620
2	1,638	1961	B & W	P	(b)	(a)	13.1	200	17	AW	5.4 4.9	Y	OB (a)A	O G	112.0 91.8	(a) (a)	18.0 109	1,743 1,666	7 7	24 24	700 660	(a) (a)	240 233	340 410
2	1,560	1959	B & W	P	(b)	(a)	(a)	203	(a)	FW	5.4 6.2	Y	OB (a)A	O G	(a) 33.5	4,586 27,974	18.0 103	1,844 1,752	7 7	24 24	642 643	(a) (a)	249 249	440 620

(a) Data not reported.
(b) Not applicable.
(c) Initial year of operation for 2 or more boilers indicate the earliest and latest initial year among the group of boilers.
(d) ppm corrected to 3% oxygen in the flue gas.

Codes: Column 4 - B & W - Babcock and Wilcox
C.E. - Combustion Engineering
R - Riley

Column 11 - FW, Frontwall; HO, Horizontally Opposed; CY, Cyclone; T, Tangential; AW, All Wall Fired.

Column 13 - Y, Yes; N, No

APPENDIX 3-6

Summary of NO_x Emissions from 21 Urban Areas(1)

This summary provides NO_x emission data classified by major stationary and mobile sources on 21 urban areas. For ready comparison purposes, the NO_x emissions in pounds per capita-year from stationary and total sources are listed. These urban areas had a total population of about 44 million in the year 1967, or about one-fifth of total U.S. population.

Total NO_x emission per capita-year vary from a low of 61 pounds in Niagara County, New York, to a high of 480 pounds in Northwest Indiana. The latter area (East Chicago, Gary, Hammond and Whiting) includes a heavy industrial complex of three large steel mills, four large refineries, two power plants, a large cement plant as well as foundries, steel fabricators and chemical plants. The average NO_x emission rate for the 21 areas was 126 pounds per capita-year compared to about 149 pounds per capita-year for the entire United States.

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(1) Urban Area Pollution Surveys from Air Quality and Emission Data Division, NAPCA. Durham, North Carolina, 1968 and 1969.

APPENDIX 3-6 (CONT'D.)

SUMMARY OF NO_x EMISSIONS FROM 21 URBAN AREAS(1)

				NO_x Emissions - 10^3 Tons Per Year											
				Stationary Sources						Mobile Sources				Grand Total	
Urban Area	Year	Area (Sq. Miles)	Population Million	Household & Commercial	Industry	Power Plants	Refuse	Total (Rounded)	Pounds Per Capita-Year	Pass. Motor	Trucks, Buses, Etc.	Aircraft	Total (Rounded)	10^3 Tons (Rounded)	Pounds Per Capita-Year
1. Los Angeles County	1969	4,083	7.3	18.3	43.8	51.1	0.4	114	31	230	5.9	5.5	241	355	97
2. Pittsburgh, Pa. (SMSA)	1967	3,054	2.5	14.4	123.1	76.5	5.2	219	174	46	--	4.6	51	267	212
3. Louisville, Kty.	1967	1,392	0.8	4.1	17.6	3.7	0.6	26	62	15	--	2.4	17	44	104
4. Dallas-Ft. Worth, Texas	1967	7,988	2.2	4.4	5.1	19.6	1.8	30	27	53	8.9	2.6	65	95	87
5. Seattle-Tacoma (SMSA)	1967	15,000	2.0	3.3	13.6	--	4.2	21	21	52	3.8	--	56	76	76
6. St. Louis, Mo.	1967	4,499	2.4	13.1	36.5	72.4	2.2	124	104	50	6.1	--	56	181	150
7. Boston, Mass. (SMSA)	1967	1,280	2.7	69.2	12.7	43.1	9.8	135	100	41	2.5	1.8	45	180	133
8. Cincinnati, Hamilton, Middletown	1967	2,620	1.7	10.6	22.0	61.0	1.7	95	115	24	9.3	0.8	34	130	156
9. Northwest Indiana	1965	85	0.4	3.4	59.7	25.3	--	88	440	--	--	--	8	96	480
10. Buffalo, N.Y. (SMSA)	1967	--	1.3	4.3	74.9	16.0	--	95	144	28	1.5	0.5	30	125	189
11. Delaware Valley	1965	4,565	5.6	51.1	107.3	101.8	2.6	263	94	85	12.0	2.2	99	362	129
12. Akron and Barberton	1963	--	0.3	2.2	20.8	2.2	--	25	153	--	--	--	7	32	194
13. Bay Area, Calif.	1967	--	4.3	9.7	30.8	33.4	0.4	74	35	102	11.0	--	113	187	87
14. Niagara County, N.Y.	1961	562	0.2	2.2	3.9	--		6	52	1	0.1	--	1	7	61
15. Providence Area, R.I.	1967	1,000	1.2	2.5	3.5	31.5	2.9	42	71	22	0.6	--	22	64	107
16. Dayton, Ohio	1967	2,313	0.9	4.4	14.0	21.1	1.8	41	94	17	2.6	0.6	20	61	140
17. Indianapolis, Indiana	1967	3,080	1.0	5.4	14.1	18.3	3.6	41	83	23	3.6	0.5	27	69	138
18. San Antonio, Texas	1968	7,300	1.0	1.2	2.1	8.5	0.6	12	139	20	3.5	3.7	27	40	81
19. Washington, D.C.	1967	2,045	2.5	31.5	1.5	48.4	0.9	82	66	48	3.5	1.0	53	135	108
20. Houston, Galveston	1967	7,800	2.0	2.2	112.9	44.0	4.8	163	163	41	6.7	1.5	49	212	213
21. Milwaukee, Racine, Kenosha	1967	2,628	1.7	6.5	48.6	10.8	3.9	66	78	34	7.1	--	41	107	126
TOTALS			44.0					1,764	80					2,762	126

(1) Urban area pollution surveys from Air Quality and Emission Data Division, NAPCA, Durham, North Carolina.

APPENDIX 3-7

SUMMARY OF PETROLEUM AND NATURAL GAS INDUSTRY SURVEY - 1967

	Fuel	Consuming Unit	Size 10^6 BTU/Hr	Size HP	Size Average HP	Annual Fuel Consumption(1)	Emission Factor(2)	NO_x Emission Thousand Tons/Yr.
Oil & Gas Production								
	Diesel Oil	Driver		All Sizes		7.3	9.3	34
	Gas	Furnace	All Sizes			495	0.20	50
	Gas	Driver		All Sizes		124	0.77	48
Subtotal								132
Gas Plants								
	Gas	Process Heaters	0-110	--		58	0.16	5
	Gas	Process Heaters	100-200	--		70	0.23	8
	Gas	Steam Generators	41 (av.)	--		119	0.18	11
	Gas	Gas Engine		0-300	80	54	0.77	21
	Gas	Gas Engine		301-1799	777	161	4.08	328
	Gas	Gas Engine		1800+	2121	45	9.4	212
	Gas	Gas Turbine		301-1799	1193	8	0.2	1
	Gas	Gas Turbine		1800+	3624	7	0.2	1
Subtotal								587
Pipelines								
	Gas	Gas Engine		1300 (av.)		436	7.32	1596
		Gas Turbine		5200 (av.)		140	0.2	14
Subtotal								1610
Refining								
	Gas	Process Furnaces	0-100			579	0.18	52
	Gas	Process Furnaces	100-200			309	0.22	34
	Gas	Process Furnaces	200-300			112	0.23	13
	Gas	Process Furnaces	300+			152	0.25	19
	Gas	Steam Boilers	134 (av.)			425	0.22	47
	Gas	CO Boiler (Aux. Fuel)				79	(3)	
	Gas	Gas Engines		0-300	227	5	1.64	4
	Gas	Gas Engines		301-1799	612	28	3.6	50
	Gas	Gas Engines		1800+	4180	7	9.4	33
	Gas	Gas Turbine		1800+	9379	54	0.2	5
	Oil	Process Furnaces	0-100			7.9	2.3	9
	Oil	Process Furnaces	100-200			6.5	2.9	9
	Oil	Process Furnaces	200-300			4.9	3.1	8
	Oil	Process Furnaces	300+			0.3	3.5	1
	Oil	Steam Generators	134 (av.)			18.6	2.9	27
	Oil	CO Boilers (Aux. Fuel)	221 (av.)			1.5	(3)	--
	Coal	Steam Generators	134 (av.)			8.6	20	~0
	Coke	Cat. Plant Regen.	295 (av.)			9600	4.2	3
	CO	CO Boiler	221 (av.)			134	0.23	15
Subtotal								330
							GRAND TOTAL	2659

(1) Oil consumption as million barrels.
Gas consumption as billion standard cubic feet.
Coal or coke as thousand tons.
CO consumption as trillion BTU.

(2) Oil emission factor - pounds NO_x per barrel.
Gas emission factor - pounds NO_x per thousand standard cubic feet.
Coal emission factor - pounds NO_x per ton.
CO boiler emission factor - pounds NO_x per million BTU.
Coke emission factor - pounds NO_x per thousand barrels feed.

(3) Included in CO boiler.

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APPENDIX 8-1

COMBUSTION MODIFICATION CONTROL COSTS

Public Utility Boilers - 1980

Plant Size - 1000MW; Fuel - Gas; Load Factor - 6120 Hrs/Yr

Control Method	Fixed Costs			Operating Costs		Total Costs Per Year $1000
	Start-Up Costs $1000	Capital Equipment Costs $1000	Capital Charges $1000	Maintenance Supplies and Overhead $1000	Other Operating Costs $1000	
	(1)	(2)	(3)	(4)	(5)	(6)
Low Excess Air	Assumed Negligible Compared to Capital Equipment Costs	0 120 120	17	0 21 21	-133	-95
2-Stage Combustion		0	0	0	0	0
Low Excess Air + 2-Stage Combustion		120	17	21	-133	-95
Flue Gas Recirculation		600	84	52	66	202
Low Excess Air + Flue Gas Recirculation		720	101	73	-67	107
Water Injection		23	3	2	139	144

APPENDIX 8-2

COMBUSTION MODIFICATION CONTROL COSTS

Public Utility Boilers - 1980

Plant Size - 1000MW; Fuel - Oil; Load Factor - 6120 Hrs/Yr

Control Method	Fixed Costs			Operating Costs		Total Costs Per Year $1000 (6)
	Start-Up Costs $1000 (1)	Capital Equipment Costs $1000 (2)	Capital Charges $1000 (3)	Maintenance Supplies and Overhead $1000 (4)	Other Operating Costs $1000 (5)	
Low Excess Air	Assumed Negligible Compared to Capital Equipment Costs	0 120 120	17	0 21 21	-335	-297
2-Stage Combustion		0	0	0	0	0
Low Excess Air + 2-Stage Combustion		120	17	21	-335	-297
Flue Gas Recirculation		600	84	52	66	202
Low Excess Air + Flue Gas Recirculation		720	101	73	-269	-95
Water Injection		23	3	2	174	179

APPENDIX 8-3

COMBUSTION MODIFICATION CONTROL COSTS

Public Utility Boilers - 1980

Plant Size - 1000MW; Fuel - Coal; Load Factor - 6120 Hrs/Yr

Control Method	Fixed Costs			Operating Costs		
	Start-Up Costs $1000	Capital Equipment Costs $1000	Capital Charges $1000	Maintenance Supplies and Overhead $1000	Other Operating Costs $1000	Total Costs Per Year $1000
	(1)	(2)	(3)	(4)	(5)	(6)
Low Excess Air	Assumed Negligible Compared to Capital Equipment Costs	360 120 480	67	31 21 52	-198	-79
2-Stage Combustion		1900	266	33	0	299
Low Excess Air + 2-Stage Combustion		2380	333	85	-198	220
Flue Gas Recirculation		600	84	52	66	202
Low Excess Air + Flue Gas Recirculation		1080	151	104	-132	123
Water Injection		23	3	2	138	143

APPENDIX 8-4

COMBUSTION MODIFICATION CONTROL COSTS

Public Utility Boilers - 1980

Plant Size - 750MW; Fuel - Gas; Load Factor - 6120 Hrs/Yr

Control Method	Fixed Costs			Operating Costs		
	Start-Up Costs $1000 (1)	Capital Equipment Costs $1000 (2)	Capital Charges $1000 (3)	Maintenance Supplies and Overhead $1000 (4)	Other Operating Costs $1000 (5)	Total Costs Per Year $1000 (6)
Low Excess Air	Assumed Negligible Compared to Capital Equipment Costs	19 100 119	17	2 17 19	-104	-68
2-Stage Combustion		153	21	3	0	24
Low Excess Air + 2-Stage Combustion		272	38	21	-104	-45
Flue Gas Recirculation		490	69	42	49	160
Low Excess Air + Flue Gas Recirculation		609	85	61	-55	91
Water Injection		19	3	2	109	114

APPENDIX 8-5

COMBUSTION MODIFICATION CONTROL COSTS

Public Utility Boilers - 1980

Plant Size - 750MW; Fuel - Oil; Load Factor - 6120 Hrs/Yr

Control Method	Fixed Costs			Operating Costs		Total Costs Per Year $1000
	Start-Up Costs $1000	Capital Equipment Costs $1000	Capital Charges $1000	Maintenance Supplies and Overhead $1000	Other Operating Costs $1000	
	(1)	(2)	(3)	(4)	(5)	(6)
Low Excess Air	Assumed Negligible Compared to Capital Equipment Costs	19 100 119	17	2 17 19	-262	-226
2-Stage Combustion		153	21	3	0	24
Low Excess Air + 2-Stage Combustion		272	38	21	-262	-203
Flue Gas Recirculation		490	69	42	49	160
Low Excess Air + Flue Gas Recirculation		609	85	61	-213	-67
Water Injection		19	3	2	136	141

APPENDIX 8-6

COMBUSTION MODIFICATION CONTROL COSTS

Public Utility Boilers - 1980

Plant Size - 750MW; Fuel - Coal; Load Factor - 6120 Hrs/Hr

Control Method	Fixed Costs			Operating Costs		Total Costs Per Year $1000 (6)
	Start-Up Costs $1000 (1)	Capital Equipment Costs $1000 (2)	Capital Charges $1000 (3)	Maintenance Supplies and Overhead $1000 (4)	Other Operating Costs $1000 (5)	
Low Excess Air	Assumed Negligible Compared to Capital Equipment Costs	285 100 385	54	25 17 42	-155	-59
2-Stage Combustion		1530	214	26	0	240
Low Excess Air + 2-Stage Combustion		1915	268	68	-155	181
Flue Gas Recirculation		490	69	42	49	160
Low Excess Air + Flue Gas Recirculation		875	123	84	-106	101
Water Injection		19	3	2	108	113

APPENDIX 8-7

COMBUSTION MODIFICATION CONTROL COSTS

Public Utility Boilers - 1980

Plant Size - 500MW; Fuel - Gas; Load Factor - 5260 Hrs/Yr

Control Method	Fixed Costs			Operating Costs		Total Costs Per Year $1000
	Start-Up Costs $1000	Capital Equipment Costs $1000	Capital Charges $1000	Maintenance Supplies and Overhead $1000	Other Operating Costs $1000	
	(1)	(2)	(3)	(4)	(5)	(6)
Low Excess Air	Assumed Negligible Compared to Capital Equipment Costs	34 72 106	15	3 12 15	-65	-35
2-Stage Combustion		280	39	5	0	44
Low Excess Air + 2-Stage Combustion		386	54	20	-65	9
Flue Gas Recirculation		360	50	31	28	109
Low Excess Air + Flue Gas Recirculation		466	65	46	-37	74
Water Injection		14	2	1	68	71

APPENDIX 8-8

COMBUSTION MODIFICATION CONTROL COSTS

Public Utility Boilers - 1980

Plant Size - 500MW; Fuel - Oil; Load Factor - 5260 Hrs/Yr

Control Method	Fixed Costs			Operating Costs		Total Costs Per Year $1000 (6)
	Start-Up Costs $1000 (1)	Capital Equipment Costs $1000 (2)	Capital Charges $1000 (3)	Maintenance Supplies and Overhead $1000 (4)	Other Operating Costs $1000 (5)	
Low Excess Air	Assumed Negligible Compared to Capital Equipment Costs	34 72 106	15	3 12 15	-162	-132
2-Stage Combustion		280	39	5	0	44
Low Excess Air + 2-Stage Combustion		386	54	20	-162	-88
Flue Gas Recirculation		360	50	31	28	109
Low Excess Air + Flue Gas Recirculation		466	65	46	-134	-23
Water Injection		14	2	1	84	87

APPENDIX 8-9

COMBUSTION MODIFICATION CONTROL COSTS

Public Utility Boilers - 1980

Plant Size - 500MW; Fuel - Coal; Load Factor - 5260 Hrs/Hr

Control Method	Fixed Costs			Operating Costs		
	Start-Up Costs $1000	Capital Equipment Costs $1000	Capital Charges $1000	Maintenance Supplies and Overhead $1000	Other Operating Costs $1000	Total Costs Per Year $1000
	(1)	(2)	(3)	(4)	(5)	(6)
Low Excess Air	Assumed Negligible Compared to Capital Equipment Costs	203 72 275	39	18 12 30	-96	-27
2-Stage Combustion		1120	157	19	0	176
Low Excess Air + 2-Stage Combustion		1395	195	49	-96	148
Flue Gas Recirculation		360	50	31	28	109
Low Excess Air + Flue Gas Recirculation		635	89	61	-68	82
Water Injection		14	2	1	67	70

APPENDIX 8-10

COMBUSTION MODIFICATION CONTROL COSTS

Public Utility Boilers - 1980

Plant Size - 250MW; Fuel - Gas; Load Factor - 3942 Hrs/Yr

Control Method	Fixed Costs			Operating Costs		
	Start-Up Costs $1000 (1)	Capital Equipment Costs $1000 (2)	Capital Charges $1000 (3)	Maintenance Supplies and Overhead $1000 (4)	Other Operating Costs $1000 (5)	Total Costs Per Year $1000 (6)
Low Excess Air	Assumed Negligible Compared to Capital Equipment Costs	39 43 82	11	4 7 11	-26	-4
2-Stage Combustion		330	46	6	0	52
Low Excess Air + 2-Stage Combustion		412	58	17	-26	49
Flue Gas Recirculation		210	29	18	11	58
Low Excess Air + Flue Gas Recirculation		292	41	29	-15	55
Water Injection		8	1	1	27	29

APPENDIX 8-11

COMBUSTION MODIFICATION CONTROL COSTS

Public Utility Boilers - 1980

Plant Size - 250MW; Fuel - Oil; Load Factor - 3942 Hrs/Yr

Control Method	Fixed Costs			Operating Costs		Total Costs Per Year $1000 (6)
	Start-Up Costs $1000 (1)	Capital Equipment Costs $1000 (2)	Capital Charges $1000 (3)	Maintenance Supplies and Overhead $1000 (4)	Other Operating Costs $1000 (5)	
Low Excess Air	Assumed Negligible Compared to Capital Equipment Costs	39 43 82	11	4 7 11	-66	-44
2-Stage Combustion		330	46	6	0	52
Low Excess Air + 2-Stage Combustion		412	58	17	-66	9
Flue Gas Recirculation		210	29	18	11	58
Low Excess Air + Flue Gas Recirculation		292	41	29	-55	15
Water Injection		8	1	1	34	36

APPENDIX 8-12

COMBUSTION MODIFICATION CONTROL COSTS

Public Utility Boilers - 1980

Plant Size - 250MW; Fuel - Coal; Load Factor - 3942 Hrs/Yr

Control Method	Fixed Costs			Operating Costs		Total Costs Per Year $1000
	Start-Up Costs $1000	Capital Equipment Costs $1000	Capital Charges $1000	Maintenance Supplies and Overhead $1000	Other Operating Costs $1000	
	(1)	(2)	(3)	(4)	(5)	(6)
Low Excess Air	Assumed Negligible Compared to Capital Equipment Costs	116 43 159	22	10 7 17	-39	0
2-Stage Combustion		660	92	11	0	103
Low Excess Air + 2-Stage Combustion		819	115	28	-39	104
Flue Gas Recirculation		210	29	18	11	58
Low Excess Air + Flue Gas Recirculation		369	52	35	-28	59
Water Injection		8	1	1	27	29

APPENDIX 8-13

COMBUSTION MODIFICATION CONTROL COSTS

Public Utility Boilers - 1980

Plant Size - 120MW; Fuel - Gas; Load Factor - 2190 Hrs/Yr

Control Method	Fixed Costs			Operating Costs		Total Costs Per Year $1000
	Start-Up Costs $1000	Capital Equipment Costs $1000	Capital Charges $1000	Maintenance Supplies and Overhead $1000	Other Operating Costs $1000	
	(1)	(2)	(3)	(4)	(5)	(6)
Low Excess Air	Assumed Negligible Compared to Capital Equipment Costs	38 25 63	9	8	-7	10
2-Stage Combustion		342	48	6	0	54
Low Excess Air + 2-Stage Combustion		405	57	14	-7	64
Flue Gas Recirculation		120	17	10	3	24
Low Excess Air + Flue Gas Recirculation		183	26	18	-4	40
Water Injection		5	1	0	8	9

APPENDIX 8-14

COMBUSTION MODIFICATION CONTROL COSTS

Public Utility Boilers - 1980

Plant Size - 120MW; Fuel - Oil; Load Factor - 2190 Hrs/Yr

Control Method	Fixed Costs			Operating Costs		Total Costs Per Year $1000 (6)
	Start-Up Costs $1000 (1)	Capital Equipment Costs $1000 (2)	Capital Charges $1000 (3)	Maintenance Supplies and Overhead $1000 (4)	Other Operating Costs $1000 (5)	
Low Excess Air	Assumed Negligible Compared to Capital Equipment Costs	38 25 63	9	8	-19	-2
2-Stage Combustion		342	48	6	0	54
Low Excess Air + 2-Stage Combustion		405	57	14	-19	52
Flue Gas Recirculation		120	17	10	3	30
Low Excess Air + Flue Gas Recirculation		183	26	18	-16	28
Water Injection		5	1	0	10	11

APPENDIX 8-15

COMBUSTION MODIFICATION CONTROL COSTS

Public Utility Boilers - 1980

Plant Size - 120MW; Fuel - Coal; Load Factor - 2190 Hrs/Yr

Control Method	Fixed Costs			Operating Costs		
	Start-Up Costs $1000	Capital Equipment Costs $1000	Capital Charges $1000	Maintenance Supplies and Overhead $1000	Other Operating Costs $1000	Total Costs Per Year $1000
	(1)	(2)	(3)	(4)	(5)	(6)
Low Excess Air	Assumed Negligible Compared to Capital Equipment Costs	63 25 88	12	10	-11	11
2-Stage Combustion		380	53	7	0	60
Low Excess Air + 2-Stage Combustion		468	66	17	-11	72
Flue Gas Recirculation		120	17	10	3	30
Low Excess Air + Flue Gas Recirculation		208	29	20	-8	41
Water Injection		5	1	0	8	9

APPENDIX 8-16

INDUSTRIAL AND COMMERCIAL BOILERS - 1980

Gas - 4280 Hr.
Oil - 4530 Hr.

Estimated NO_x Control Costs - 27,700 Lb Steam/Hr Water Tube Boiler

Control Method	Fixed Costs			Operating Costs				Total Costs Per Year $1000 (6)	
	Start-Up Costs $1000 (1)	Capital Equipment Costs $1000 (2)	Capital Charges $1000 (3)	Maintenance, Supplies and Overhead $1000 (4)		Other Operating Costs $1000 (5)			
						Gas	Oil	Gas	Oil
Low Excess Air	0.6	3.0	0.462	17.3%	.0798	-.349 .425 -.076	-.454 .425 -.029	.6178	.5128
Flue Gas Recirculation (Fan Size) 40 HP	0.6	8.0	1.16	8.63%	0.100	.765	.811	2.025	2.071
Low Excess Air + Flue Gas Recirculation	1.2	11.0	1.62		.1798	.841	.782	2.641	2.582
Water Injection	0.2	1.8	.258	8.63%	.022	.349	.454	.629	.734

APPENDIX 8-17

INDUSTRIAL AND COMMERCIAL BOILERS - 1980

Gas - 4330 Hr.
Oil - 4510 Hr.

Estimated NO_x Control Costs - 144,500 Lb/Steam/Hr Watertube Boiler

Control Method	Fixed Costs			Operating Costs			Total Costs Per Year $1000 (6)	
	Start-Up Costs $1000 (1)	Capital Equipment Costs $1000 (2)	Capital Charges $1000 (3)	Maintenance, Supplies and Overhead $1000 (4)	Other Operating Costs $1000 (5)			
					Gas	Oil	Gas	Oil
Low Excess Air	0.6	6.5	.952	17.3% .1645	-1.890 .700 -1.140	-2.360 .700 -1.660	-.0235	-.5435
Flue Gas Recirculation (Fan Size) 89 HP	0.6	100.0	14.0	8.63% 1.21	1.725	1.795	16.975	17.045
Low Excess Air + Flue Gas Recirculation	1.2	106.5	15.0	1.3745	.585	.135	16.9595	16.509
Water Injection	0.2	2.7	.392	8.63% .0338	1.840	2.360	2.2658	2.786

APPENDIX 8-18

INDUSTRIAL AND COMMERCIAL BOILERS - 1980

Coal - 4550 Hr.

Estimated NO_x Control Costs - 36,100 Lb Steam/Hr Watertube Boiler

Control Method	Fixed Costs			Operating Costs		Total Costs Per Year $1000 (6)
	Start-Up Costs $1000 (1)	Capital Equipment Costs $1000 (2)	Capital Charges $1000 (3)	Maintenance Supplies and Overhead $1000 (4)	Other Operating Costs $1000 (5)	
Low Excess Air	0.6	3.25	.497	17.3% .0860	Coal -.460 .425 -.035	.548
Flue Gas Recirculation (Fan Size) 55 HP	0.6	14.0	2.00	8.63% .1726	1.120	3.293
Low Excess Air + Flue Gas Recirculation	1.2	17.2	2.50	.2586	1.085	3.841
Water Injection	0.2	2.0	.294	8.63% .0254	.460	.779

APPENDIX 8-19

INDUSTRIAL AND COMMERCIAL BOILERS - 1980

Coal - 4560 Hr.

Estimated NO_x Control Costs - 187,500 Lb Steam/Hr Watertube Boiler

Control Method	Fixed Costs			Operating Costs		
	Start-Up Costs $1000	Capital Equipment Costs $1000	Capital Charges $1000	Maintenance Supplies and Overhead $1000	Other Operating Costs $1000	Total Costs Per Year $1000
	(1)	(2)	(3)	(4)	(5)	(6)
Low Excess Air	0.6	7.5	1.092	17.3% .1890	Coal -2.411 .700 -1.411	.130
Flue Gas Recirculation (Fan Size) 115 HP	0.6	1330	18.66	8.63% 1.610	2.345	22.61
Low Excess Air + Flue Gas Recirculation	1.2	140.5	19.75	1.799	.934	22.48
Water Injection	0.2	3.0	.434	8.63% .0374	2.411	2.882

APPENDIX 8-20

INDUSTRIAL AND COMMERCIAL BOILERS - 1980

Gas - 2320 Hr.
Oil - 2440 Hr.

Estimated NO_x Control Costs - 107 BHP Firetube Boiler

Control Method	Fixed Costs			Operating Costs		
	Start-Up Costs $1000	Capital Equipment Costs $1000	Capital Charges $1000	Maintenance Supplies and Overhead $1000	Other Operating Costs $1000	Total Costs Per Year $1000
	(1)	(2)	(3)	(4)	(5)	(6)
					Gas Oil	
Low Excess Air	0.6	2.0	.322	17.3% .0556	-.0267 -.0340 .425 .425 .398 .391	.7756 .7686
Flue Gas Recirculation (Fan Size) 6 HP	0.6	2.5	.392	8.63% .0338	.062 .065	.04878 .4908
Low Excess Air + Flue Gas Recirculation	1.2	4.5	.714	.0894	.460 .456	1.263 1.259
Water Injection	0.2	1.0	.154	8.63% .0133	.0267 .0340	.1940 .2013

APPENDIX 8-21

PLANT INVESTMENT COSTS FOR REMOVING NO_x FROM STACK GAS OF 1000 MW COAL OR OIL FIRED POWER PLANT USING A CATALYTIC DECOMPOSITION OR H_2 REDUCTION CONTROL SYSTEM

	Material and Labor Costs, $1,000		
	Catalyst Costs		
Equipment	$50/Ft^3	$150/Ft^3	$300/Ft^3
Reactor	652	652	652
Catalyst for Reactor	770	2309	4618
ID Fan	537	537	537
Material and Labor Sub-Total Costs	1,959	3,498	5,807
Field Labor Overhead and Burden	356	356	356
Engineering and Contracting Fees	360	360	360
Sub-Total for Contingency	2,675	4,214	6,523
Contingency	401	632	978
Working Conditions	119	210	349
Total Plant Investments	3,195	5,056	7,850
Investment Credits	0	0	0
Net Investment	3,195	5,056	7,850

APPENDIX 8-22

ANNUAL CONTROL COSTS FOR REMOVING NO$_x$ FROM STACK GAS OF 1000 MW COAL OR OIL FIRED POWER PLANT USING A CATALYTIC DECOMPOSITION CONTROL SYSTEM

	Operating Charges, $\$1,000$		
	Catalyst Costs		
	$\$50/\text{Ft}^3$	$\$150/\text{Ft}^3$	$\$300/\text{Ft}^3$
Capital Charges	447	708	1,099
Maintenance	160	253	393
Supplies	24	38	59
Direct Labor			
Supervision			
Payroll Burden			
Plant Overhead	92	146	226
Utilities			
Electricity	235	235	235
Steam			
Process Water			
Cooling Water			
Fuels			
Chemicals			
Catalysts	385	1,155	2,309
Total Costs	1,343	2,535	4,321
Credits			
Total Credits	0	0	0
Total Annual Operating Costs	1,343	2,535	4,321
$\$$/Ton NO$_x$ Removed (calculated as NO$_2$)	50	94	160
mils/KWH	0.22	0.41	0.71
$\$$/Ton Coal Fired	0.63	1.18	2.02

APPENDIX 8-23

PLANT INVESTMENT COSTS FOR REMOVING NO_x FROM STACK GAS OF 1000 MW GAS FIRED POWER PLANT USING A CATALYTIC DECOMPOSITION OR H_2 OR NH_3 REDUCTION CONTROL SYSTEM

Equipment	Material and Labor Costs, $1,000 Catalyst Cost $50/Ft^3	 $150/Ft^3	 $300/Ft^3
Reactor	652	652	652
Catalyst for Reactor	770	2309	4618
ID Fan	440	440	440
Material and Labor Sub-Total Costs	1,862	3,401	5,710
Field Labor Overhead and Burden	340	340	340
Engineering and Contracting Fees	350	350	350
Sub-Total for Contingency	2,552	4,091	6,400
Contingency	383	614	960
Working Conditions	112	204	343
Total Plant Investments	3,047	4,909	7,703
Investment Credits	0	0	0
Net Investment	3,047	4,909	7,703

APPENDIX 8-24

ANNUAL CONTROL COSTS FOR REMOVING NO_x FROM STACK GAS OF 1000 MW GAS FIRED POWER PLANT USING A CATALYTIC DECOMPOSITION CONTROL SYSTEM

	Operating Charges, \$1,000		
	Catalyst Costs		
	\$50/Ft^3	\$150/Ft^3	\$300/Ft^3
Capital Charges	427	687	1,078
Maintenance	152	245	385
Supplies	23	37	58
Direct Labor			
Supervision			
Payroll Burden			
Plant Overhead	88	141	222
Utilities			
Electricity	184	184	184
Steam			
Process Water			
Cooling Water			
Fuels			
Chemicals			
Catalysts	257	770	1,539
Total Costs	1,131	2,064	3,466
Credits			
Total Credits	0	0	0
Total Annual Operating Costs	1,131	2,064	3,466
\$/Ton NO_x Removed (calculated as NO_2)	24	43	73
mils/KWH	0.18	0.34	0.57

APPENDIX 8-25

ANNUAL CONTROL COSTS FOR REMOVING NO_x FROM STACK GAS OF 1000 MW COAL OR OIL FIRED POWER PLANT USING A SELECTIVE H_2 REDUCTION CONTROL SYSTEM

	Operating Charges, $1,000		
	Catalyst Costs		
	$50/Ft^3	$150/Ft^3	$300/Ft^3
apital Charges *	447	708	1,099
Maintenance	160	253	393
upplies	24	38	59
irect Labor	26	26	26
Supervision	4	4	4
Payroll Burden	6	6	6
ant Overhead	107	161	241
tilities			
Electricity	235	235	235
Steam			
Process Water			
Cooling Water			
uels			
emicals	199	199	199
Catalysts	385	1,156	2,309
Total Costs	1,593	2,786	4,571
Credits	-	--	--
Total Credits			
Total Annual Operating Costs	1,593	2,786	4,571
$/Ton NO_x Removed (Calculated as NO_2)	59	103	169
mils/KWH	0.26	0.46	0.75
$/Ton Coal Fired	0.74	1.30	2.13

* Investment costs are same as for catalytic decomposition (Appendix 8-1)

APPENDIX 8-26

ANNUAL CONTROL COSTS FOR REMOVING NO_x FROM STACK GAS OF 1000 MW GAS FIRED POWER PLANT USING A SELECTIVE H_2 REDUCTION CONTROL SYSTEM

	Operating Charges, $1,000		
	Catalyst Costs		
	$50/Ft^3	$150/Ft^3	$300/Ft^3
Capital Charges *	427	687	1,078
Maintenance	152	245	385
Supplies	23	37	58
Direct Labor	26	26	26
Supervision	4	4	4
Payroll Burden	6	6	6
Plant Overhead	103	156	237
Utilities			
Electricity	184	184	184
Steam			
Process Water			
Cooling Water			
Fuels			
Chemicals	350	350	350
Catalysts	257	770	1,539
Total Costs	1,532	2,465	3,867
Credits	--	--	--
Total Credits	0	0	0
Total Annual Operating Costs	1,532	2,465	3,867
\$/Ton NO_x Removed (Calculated as NO_2)			
mils/KWH	0.25	0.40	0.63

* Investment costs are same as for catalytic decomposition (Appendix 8-2)

APPENDIX 8-27

ANNUAL CONTROL COSTS FOR REMOVING NO_x FROM STACK GAS OF 1000 MW GAS FIRED POWER PLANT USING AN NH_3 REDUCTION AND SCRUBBING SYSTEM

	Operating Charges, $1,000		
	Catalyst Costs		
	$50/Ft^3	$150/Ft^3	$300/Ft^3
Capital Charges *	427	687	1,078
Maintenance	152	245	385
Supplies	23	37	58
Direct Labor	26	26	52
Supervision	4	4	8
Payroll Burden	6	6	12
Plant Overhead	103	156	252
Utilities			
Electricity	184	184	184
Steam			
Process Water			
Cooling Water			
Fuels			
Chemicals	412	412	412
Catalysts	257	770	1,539
Total Costs	1,594	2,527	3,980
Credits	--	--	--
Total Credits			
Total Annual Operating Costs	1,594	2,527	3,980
\$/Ton NO_x Removed (Calculated as NO_2)			
mils/KWH	0.26	0.41	0.65

* Investment costs are same as for catalytic decomposition (Appendix 8-3)

APPENDIX 8-28

PLANT INVESTMENT COSTS FOR REMOVING NO_x FROM STACK GAS OF 1000 MW COAL-FIRED POWER PLANT USING CATALYTIC NH_3 PROCESS FOR NO_x AND SO_x EMISSION CONTROL

	Material and Labor Costs, $1,000		
	Catalyst Costs		
Equipment	$50/Ft^3	$150/Ft^3	$300/Ft^3
Reducing Reactor	<——	652	——>
Catalyst for Reducing Reactor	770	2,309	4,618
Scrubber	<——	2,700	——>
Recirculating Pumps	<——	219	——>
Mixing Tanks	<——	252	——>
Oxidizer Tank	<——	66	——>
Evaporator Crystallizer	<——	848	——>
Pumps	<——	110	——>
Centrifuge and Rotary Cooler	<——	345	——>
$(NH_4)_2SO_4$ Storage/Handling System	<——	723	——>
$(NH_4)_2SO_4$ Cyclones	<——	6	——>
Air Compressor	<——	417	——>
ID Fan off Cyclones	<——	16	——>
ID Fan for Flue Gas	<——	694	——>
Duct Work	<——	304	——>
Stack Gas Reheater Burner	<——	825	——>
Material and Labor Sub-Total Costs	8,947	10,486	12,795
Field Labor Overhead and Burden	<——	1,737	——>
Engineering and Contracting Fees	<——	1,122	——>
Sub Total for Contingency	11,806	13,345	15,654
Contingency	1,771	2,001	2,348
Working Capital	537	629	768
Total Plant Investments	14,114	15,975	18,770
Investment Credits	<——	0	——>
Net Investment	14,114	15,975	18,770

APPENDIX 8-29

ANNUAL CONTROL COSTS FOR REMOVING
NO_x FROM STACK GAS OF 1000 MW COAL FIRED POWER PLANT
USING CATALYTIC NH_3 PROCESS FOR NO_x AND SO_x EMISSION CONTROL

	Operating Charges, $1,000		
	Catalyst Costs		
	$50/Ft^3	$150/Ft^3	$300/Ft^3
Capital Charges	1,976	2,237	2,628
Maintenance	706	799	938
Supplies	106	120	141
Direct Labor	79	79	79
Supervision	12	12	12
Payroll Burden	18	18	18
Plant Overhead	452	505	585
Utilities			
Electricity	626	626	626
Steam	116	116	116
Process Water	48	48	48
Cooling Water	35	35	35
Fuels	522	522	522
Chemicals	2,203	2,203	2,203
Catalysts	385	1,155	2,309
Total Costs	7,284	8,475	10,260
Credits			
$(NH_4)_2SO_4$ - 238,500 T/Y	4,770	4,770	4,770
Desulfurization and Operating Credits	1,135	1,135	1,135
Total Credits	5,905	5,905	5,905
Total Annual Operating Costs	1,379	2,570	4,355
$/Ton NOx Removed (Calculated as NO_2)	46	86	145
mils/KWH	0.23	0.42	0.71
$/Ton Coal Fired	0.64	1.20	2.03

APPENDIX 8-30

PLANT INVESTMENT COSTS FOR REMOVING NO_x FROM STACK GAS OF 1000 MW COAL-FIRED POWER PLANT USING THE PRINCETON CHEMICAL RESEARCH H_2S REDUCTION PROCESS

Equipment	**Material & Labor Costs, $1,000**
Reducing Reactors	2,400
Molecular Sieve & Alumina Catalysts	3,300
Switch Valves	530
H_2S Generators	50
H_2S Generator Preheater	32
Stripping Gas Generators	44
Stripping Gas Heater	85
Stripping Gas Blower	192
Flue Gas Cooling Chamber	198
Sulfur Cooler	56
Sulfur Scrubber	23
Ducts	135
FD Fans	694
Pumps	115
Material and Labor Sub-Total Costs	7,854
Field Labor Overhead and Burden	1,166
Engineering and Contracting Fees	727
Sub-Total for Contingency	9,747
Contingency	1,462
Working Conditions	471
Total Plant Investments	11,680
Investment Credits	0
Net Investment	11,680

APPENDIX 8-31

ANNUAL CONTROL COSTS FOR REMOVING NO_x FROM STACK GAS OF 1000 MW COAL FIRED POWER PLANT USING THE PRINCETON CHEMICAL RESEARCH H_2S REDUCTION PROCESS

	Costs $
Capital Charges	1,635,000
Maintenance	584,000
Supplies	88,000
Direct Labor	79,000
Supervision	12,000
Payroll Burden	18,000
Plant Overhead	382,000
Utilities	
Electricity	444,000
Steam	0
Process Water	13,000
Cooling Water	39,000
Fuels	508,000
Chemicals	0
Catalysts	660,000
Total Costs	4,462,000
Credits	
Sulfur 52,000 T/Y	1,300,000
Desulfurization and Operating	1,071,000
Total Credits	2,371,000
Total Annual Operating Costs	2,091,000
$/Ton NO_x Removal (calculated as NO_2)	77
mils/KWH	0.34
$/Ton Coal Fired	0.98

APPENDIX 8-32

PLANT INVESTMENT COSTS FOR REMOVING NO_x AND SO_x FROM STACK GAS OF 1000 MW COAL FIRED POWER PLANT USING A TWO SCRUBBER LIMEWATER CONTROL SYSTEM WITH ACID DECOMPOSITION

Equipment	Material and Labor Costs, $1,000
SO_2 Scrubbers	1,118
Settling Tanks	40
Recirculating Pumps	91
NO_x Scrubbers	1,118
Settling Tanks	40
Recirculating Pumps	91
Neutralizer	40
Oxidizer/HNO_3 Reactor	416
Air Blower	20
Recirculating Pumps	178
Duct Work	135
ID Fan	673
Limestone Refill and Storage Hoppers	185
Ball Mill	220
Injection System	75
Solids Disposal System	300
Stack Gas Reheater	825
Material and Labor Sub-Total Cost	5,565
Field Labor Overhead and Burden	1,205
Engineering and Contractors Fees	838
Sub-Total for Contingency	7,608
Contingency	1,141
Working Capital	334
Total Plant Investments	9,083
Investment Credits (Elimination of Electrostatic Precipitators)	1,300
Net Investment	7,783

APPENDIX 8-33

ANNUAL CONTROL COSTS FOR REMOVING NO_x AND SO_x FROM STACK GAS OF 1000 MW COAL FIRED POWER PLANT USING A TWO SCRUBBER LIMEWATER CONTROL SYSTEM WITH ACID DECOMPOSITION

	Costs $
Capital Charges	1,090,000
Maintenance	389,000
Supplies	58,000
Direct Labor	79,000
Supervision	12,000
Payroll Burden	18,000
Plant Overhead	269,000
Utilities	
Electricity	428,000
Steam	0
Process Water	28,000
Cooling Water	0
Fuels	
Chemicals	522,000
Catalysts	1,358,000
Total Costs	4,258,000
Credits	
HNO_3 - 6,450 T/Y	323,000
Desulfurization and Operating Credits	1,135,000
Total Credits	1,458,000
Total Annual Operating Costs	2,800,000
\$/Ton NO_x Removed (calculated as NO_2)	117
mils/KWH	0.46
\$/Ton Coal Fired	1.31

APPENDIX 8-34

PLANT INVESTMENT COSTS FOR REMOVING NO_x AND SO_x FROM STACK GAS OF 1000 MW COAL FIRED POWER PLANT USING A TWO SCRUBBER LIMEWATER CONTROL SYSTEM WITH THERMAL DECOMPOSITION

Equipment	Material and Labor Costs, \$1,000
SO_2 Scrubbers	1,118
Settling Tanks	40
Recirculating Pumps	91
NO_x Scrubbers	1,118
Settling Tanks	40
Recirculating Pumps	91
Evaporator	570
Decomposer	246
Oxidizer/HNO_3 Reactor	532
Mixing Tanks	6
Steam Drum	15
Air Compressor	322
Recirculating Pumps	235
HNO_3 Storage Tank	309
Heat Exchangers	151
Duct Work	135
ID Fan	673
Limestone Storage and Refill Hoppers	150
Ball Mill	165
Injection System	60
Solids Disposal System	225
Stack Gas Reheater	825
Miscellaneous	125
Material and Labor Sub-Total	7,242
Field Labor Overhead and Burden	1,521
Engineering and Contractors Fees	1,018
Sub-Total for Contingency	9,781
Contingency	1,467
Working Capital	435
Total Plant Investments	11,683
Investment Credits (Elimination of Electrostatic Precipitators)	1,300
Net Investment	10,383

APPENDIX 8-35

ANNUAL CONTROL COSTS FOR REMOVING NO_x AND SO_x FROM STACK GAS OF 1000 MW COAL FIRED POWER PLANT USING A TWO SCRUBBER LIMEWATER CONTROL SYSTEM WITH THERMAL DECOMPOSITION

	Costs $
Capital Charges	1,454,000
Maintenance	519,000
Supplies	78,000
Direct Labor	79,000
Supervision	12,000
Payroll Burden	18,000
Plant Overhead	344,000
Utilities	
Electricity	521,000
Steam	0
Process Water	47,000
Cooling Water	41,000
Fuels	978,000
Chemicals	471,000
Catalysts	10,000
Total Costs	4,572,000
Credits	
HNO_3 - 32,850 T/Y	1,643,000
Steam - 19,950 lbs/hr	58,000
Desulfurization and Operating Credits	1,200,000
Total Credits	2,901,000
Total Annual Operating Costs	1,671,000
\$/Ton NO_x Removed (calculated as NO_2)	70
mils/KWH	0.27
\$/Ton Coal Fired	0.78

APPENDIX 8-36

PLANT INVESTMENT COSTS FOR REMOVING NO$_x$ FROM STACK GAS OF 1000 MW COAL FIRED POWER PLANT USING A SINGLE SCRUBBER LIMEWATER CONTROL SYSTEM WITH THERMAL DECOMPOSITION

Equipment	Material and Labor Costs, \$1,000
Spray Cooling Towers	175
SO_2/NO_x Scrubbers	1,117
Settling Tanks	40
Recirculating Pumps	91
Evaporator	570
Decomposer	246
Oxidizer/HNO_3 Reactor	532
Mixing Tank	6
Steam Drum	15
Air Compressors	322
Recirculating Pumps	235
HNO_3 Storage Tank	309
Heat Exchangers	151
Duct Work	135
ID Fan	521
Limestone Storage and Refill Hoppers	150
Ball Mill	165
Injection System	60
Solids Disposal System	225
Stack Gas Reheater	825
Miscellaneous	126
Material and Labor Sub-Total Costs	6,016
Field Labor Overhead and Burden	1,283
Engineering and Contracting Fees	885
Sub-Total for Contingency	8,184
Contingency	1,228
Working Capital	360
Total Plant Investments	9,772
Investment Credits (Elimination of Electrostatic Precipitators)	1,300
Net Investment	8,472

APPENDIX 8-37

ANNUAL CONTROL COSTS FOR REMOVING NO_x FROM STACK GAS OF 1000 MW COAL FIRED POWER PLANT USING A SINGLE SCRUBBER LIMEWATER CONTROL SYSTEM WITH THERMAL DECOMPOSITION

	Costs $
Capital Charges	1,186,000
Maintenance	424,000
Supplies	64,000
Direct Labor	79,000
Supervision	12,000
Payroll Burden	18,000
Plant Overhead	290,000
Utilities	
Electricity	352,000
Steam	0
Process Water	47,000
Cooling Water	41,000
Fuels	978,000
Chemicals	471,000
Catalysts	10,000
Total Costs	3,972,000
Credits	
HNO_3 - 32,850 T/Y	1,643,000
Steam - 19,950 lbs/hr	58,000
Desulfurization and Operating Credits	1,200,000
Total Credits	2,901,000
Total Annual Operating Costs	1,071,000
\$/Ton NO_x Removed (calculated as NO_2)	45
mils/KWH	0.18
\$/Ton Coal Fired	0.50

APPENDIX 8-38

PLANT INVESTMEN. COSTS FOR REMOVING NO_x FROM STACK GAS OF 1000 MW OIL FIRED POWER PLANT USING A SINGLE SCRUBBER LIMEWATER CONTROL SYSTEM WITH THERMAL DECOMPOSITION

Equipment	Material and Labor Costs, \$1,000
Spray Cooling Towers	175
SO_2/NO_x Scrubbers	1,117
Settling Tanks	40
Recirculating Pumps	91
Evaporator	570
Decomposer	246
Oxidizer/HNO_3 Reactor	532
Mixing Tank	6
Steam Drum	15
Air Compressors	322
Recirculating Pumps	235
HNO_3 Storage Tanks	309
Heat Exchangers	151
Duct Work	135
ID Fan	521
Limestone Storage and Refill Hoppers	109
Ball Mill	120
Injection System	43
Solids Disposal System	160
Stack Gas Reheater	525
Miscellaneous	126
Material and Labor Costs	5,548
Field Labor Overhead and Burden	1,160
Engineering and Contracting Fees	838
Sub-Total for Contingency	7,546
Contingency	1,132
Working Capital	333
Total Plant Investments	9,011
Investment Credits	0
Net Investment	9,011

APPENDIX 8-39

ANNUAL CONTROL COSTS FOR REMOVING NO_x FROM STACK GAS OF 1000 MW OIL FIRED POWER PLANT USING A SINGLE SCRUBBER LIMEWATER CONTROL SYSTEM WITH THERMAL DECOMPOSITION

	Costs $
Capital Charges	1,262,000
Maintenance	451,000
Supplies	68,000
Direct Labor	79,000
Supervision	12,000
Payroll Burden	18,000
Plant Overhead	305,000
Utilities	
Electricity	352,000
Steam	0
Process Water	39,000
Cooling Water	41,000
Fuels	1,050,000
Chemicals	335,000
Catalysts	10,000
Total Costs	4,022,000
Credits	
HNO_3 - 32,850 T/Y	1,643,000
Steam - 19,950 lbs/hr	58,000
Desulfurization Credit	1,127,000
Total Credits	2,828,000
Total Annual Operating Costs	1,194,000
\$/Ton NO_x Removed (calculated as NO_2)	50
mils/KWH	0.20

APPENDIX 8-40

PLANT INVESTMENT COSTS FOR REMOVING NO_x FROM STACK GAS OF 1000 MW GAS FIRED POWER PLANT USING A SINGLE SCRUBBER LIMEWATER CONTROL SYSTEM WITH THERMAL DECOMPOSITION

Equipment	Material and Labor Costs, $1,000
NO_x Scrubbers	1,030
Settling Tanks	37
Recirculating Pumps	91
Evaporator	830
Decomposer	361
Oxidizer/HNO_3 Reactor	785
Mixing Fan	9
Steam Drum	24
Air Compressor	475
Recirculating Pumps	340
HNO_3 Storage Tank	455
Heat Exchangers	215
Duct Work	135
ID Fan	440
Limestone Storage and Refill Hoppers	39
Ball Mill	36
Solids Disposal System	60
Stack Gas Reheater	450
Miscellaneous	200
Material and Labor Sub-Total Costs	6,012
Field Labor Overhead and Burden	1,265
Engineering and Contracting Fees	880
Sub-Total For Contingency	8,157
Contingency	1,224
Working Capital	361
Total Plant Investments	9,742
Investment Credits	0
Net Investment	9,742

APPENDIX 8-41

ANNUAL CONTROL COSTS FOR REMOVING NO_x FROM STACK GAS OF 1000 MW GAS FIRED POWER PLANT USING A SINGLE SCRUBBER LIMEWATER CONTROL SYSTEM WITH THERMAL DECOMPOSITION

	Costs $
Capital Charges	1,364,000
Maintenance	487,000
Supplies	73,000
Direct Labor	79,000
Supervision	12,000
Payroll Burden	18,000
Plant Overhead	326,000
Utilities	
Electricity	407,000
Steam	0
Process Water	33,000
Cooling Water	71,000
Fuels	958,000
Chemicals	23,000
Catalysts	18,000
Total Costs	3,869,000
Credits	
HNO_3 - 56,864 T/Y	2,843,000
Steam - 33,200 lbs/hr	97,000
Total Credits	2,940,000
Total Annual Operating Costs	929,000
$/Ton NO_x Removed (calculated as NO_2)	22
mils/KWH	0.15

APPENDIX 8-42

PLANT INVESTMENT COSTS FOR REMOVING NO_x FROM STACK GAS OF 1000 MW COAL FIRED POWER PLANT* USING A $Mg(OH)_2$ SCRUBBING CONTROL SYSTEM

Equipment	Material and Labor Costs, $1,000
Spray Cooling Towers	175
NO_x/SO_2 Scrubbers	1,117
Settling Tanks	40
Recirculating Pumps	91
Centrifuges	119
$MgSO_4$ Decomposer/Cyclones/Slide Valve	361
SO_2 Cooler	130
Nitrite Decomposer	156
Decomposer Reboiler	183
Decomposer Condenser	19
NO Oxidizer	241
Air Compressor	250
Pumps	160
ID Fan	521
Duct Work	135
$Mg(OH)_2$ Storage and Refill Hopper	65
Ball Mill	65
Solids Disposal System	75
Stack Gas Reheater	825
Material and Labor Sub-Total Costs	4,728
Field Labor Overhead and Burden	1,017
Engineering and Contractors Fees	825
Erected NH_4NO_3 Plant	2,210
Erected H_2SO_4 Plant	2,340
Sub-Total for Contingency	11,120
Contingency	1,668
Working Capital*	512
Total Plant Investment	13,300
Investment Credits (Elimination of Electrostatic Precipitator)	1,300
Net Investment	12,000

* Includes 5% of Erected Plant Costs for NH_4NO_3 and H_2SO_4 Plants.

APPENDIX 8-43

ANNUAL CONTROL COSTS FOR REMOVING NO_x FROM STACK GAS OF 1000 MW COAL FIRED POWER PLANT USING A $Mg(OH)_2$ SCRUBBING CONTROL SYSTEM

	Costs $	
Capital Charges	1,680,000	
Maintenance	600,000	
Supplies	90,000	
Direct Labor	105,000	
Supervision	16,000	
Payroll Burden	24,000	
Plant Overhead	406,000	
Utilities		
Electricity	306,000	
Steam	265,000	
Process Water	54,000	
Cooling Water	48,000	
Fuels	822,000	
Chemicals	365,000	
Catalysts	28,000	
Total Costs	4,809,000	
Credits		
NH_4NO_3 - 41,600 T/Y	1,872,000	
H_2SO_4 - 142,000 T/Y	1,988,000	
Desulfurization Credit	1,071,000	
Total Credits	4,931,000	
Total Annual Operating Costs	122,000	profit
\$/Ton NO_x Removed (calculated as NO_2)	5.1	
mils/KWH	0.02	
\$/Ton Coal Fired	0.06	

APPENDIX 8-44

PLANT INVESTMENT COSTS FOR REMOVING NO_x FROM STACK GAS OF 1000 MW OIL FIRED POWER PLANT USING A $Mg(OH)_2$ SCRUBBING CONTROL SYSTEM

Equipment	Material and Labor Costs, $1,000
Spray Cooling Towers	175
NO_x/SO_2 Scrubbers	1,117
Settling Tanks	40
Recirculating Pumps	91
Centrifuges	119
$MgSO_4$ Decomposer/Cyclones/Slide Valve	262
SO_2 Cooler	104
Nitrite Decomposer	156
Decomposer Reboiler	183
Decomposer Condenser	19
NO Oxidizer	241
Air Compressor	205
Pumps	160
ID Fan	521
Duct Work	135
$Mg(OH)_2$ Storage and Refill Hopper	47
Ball Mill	47
Solids Disposal System	54
Stack Gas Reheater	525
Material and Labor Sub-Total Costs	4,201
Field Labor Overhead and Burden	900
Engineering and Constructors Fees	750
Erected NH_4NO_3 Plant	2,210
Erected H_2SO_4 Plant	1,670
Sub-Total for Contingency	9,731
Contingency	1,460
Working Capital	446
Total Plant Investments	11,637
Investment Credits	0
Net Investment	11,637

APPENDIX 8-45

ANNUAL CONTROL COSTS FOR REMOVING NO_x FROM STACK GAS OF 1000 MW OIL FIRED POWER PLANT USING A $Mg(OH)_2$ SCRUBBING CONTROL SYSTEM

	Costs $
Capital Charges	1,629,000
Maintenance	582,000
Supplies	87,000
Direct Labor	105,000
Supervision	16,000
Payroll Burden	24,000
Plant Overhead	395,000
Utilities	
Electricity	295,000
Steam	265,000
Process Water	46,000
Cooling Water	33,000
Fuels	859,000
Chemicals	340,000
Catalysts	20,000
Total Costs	4,696,000
Credits	
NH_4NO_3 - 41,600 T/Y	1,872,000
H_2SO_4 - 89,460 T/Y	1,251,000
Desulfurization Credit	1,063,000
Total Credits	4,186,000
Total Annual Operating Costs	510,000
\$/Ton NO_x Removed (calculated as NO_2)	21
mils/KWH	0.08

APPENDIX 8-46

PLANT INVESTMENT COSTS FOR REMOVING NO_x FROM STACK GAS OF 1000 MW GAS FIRED POWER PLANT USING A $Mg(OH)_2$ SCRUBBING CONTROL SYSTEM

Equipment	Material and Labor Costs, $1,000
NO_x Scrubbers	1,030
Settling Tanks	37
Recirculating Pumps	91
Nitrite Decomposer	230
Decomposer Reboiler	271
Decomposer Condenser	29
NO Oxidizer	390
Air Compressor	370
Pumps	241
ID Fan	440
Duct Work	135
$Mg(OH)_2$ Storage and Refill Hopper	27
Ball Mill	28
Disposal of Solids	32
Stack Gas Reheat	450
Material and Labor Sub-Total Costs	3,801
Field Labor Overhead and Burden	830
Engineering and Contractors Fees	610
Erected NH_4NO_3 Plant	3,500
Sub-Total For Contingency	8,741
Contingency	1,311
Working Capital*	403
Total Plant Investment	10,455
Investment Credits	0
Net Investment	10,455

* Includes 5% of Erected Plant Costs for NH_4NO_3 Plant.

APPENDIX 8-47

ANNUAL CONTROL COSTS FOR REMOVING NO_x FROM STACK GAS OF 1000 MW GAS FIRED POWER PLANT USING A $Mg(OH)_2$ SCRUBBING CONTROL SYSTEM

	Costs $
Capital Charges	1,464,000
Maintenance	523,000
Supplies	78,000
Direct Labor	79,000
Supervision	12,000
Payroll Burden	18,000
Plant Overhead	346,000
Utilities	
Electricity	288,000
Steam	466,000
Process Water	52,000
Cooling Water	11,000
Fuels	462,000
Chemicals	524,000
Catalysts	10,000
Total Costs	4,333,000
Credits	
NH_4NO_3 73,200 T/Y	3,294,000
Total Credits	3,294,000
Total Annual Operating Costs	1,039,000
$/Ton NO_x Removed (calculated as NO_2)	25
mils/KWH	0.17

APPENDIX 8-48

ANNUAL CONTROL COSTS FOR REMOVING NO_x FROM STACK GAS OF 500 MW COAL FIRED POWER PLANT USING A $Mg(OH)_2$ SCRUBBING CONTROL SYSTEM

	Costs $
Capital Charges*	1,036,000
Maintenance*	370,000
Supplies	56,000
Direct Labor	105,000
Supervision	16,000
Payroll Burden	24,000
Plant Overhead	274,000
Utilities	
Electricity	130,000
Steam	112,000
Process Water	23,000
Cooling Water	20,000
Fuels	350,000
Chemicals	155,000
Catalysts	12,000
Total Costs	2,683,000
Credits	
NH_4NO_3 17,665 T/Y	795,000
H_2SO_4 69,215 T/Y	969,000
Desulfurization Credit	521,000
Total Credits	2,285,000
Total Annual Operating Costs	398,000
\$/Ton NO_x Removed (calculated as NO_2)	39
mils/KWH	0.08
\$/Ton Coal Fired	0.38

* Using 0.7 scaling power factor on 1000 MW plant investment.

APPENDIX 8-49

ANNUAL CONTROL COSTS FOR REMOVING NO_x FROM STACK GAS OF 120 MW COAL FIRED POWER PLANT USING A $Mg(OH)_2$ SCRUBBING CONTROL SYSTEM

	Costs $
Capital Charges*	380,000
Maintenance*	140,000
Supplies	2,000
Direct Labor	35,000
Supervision	5,000
Payroll Burden	8,000
Plant Overhead	91,000
Utilities	
Electricity	13,000
Steam	11,000
Process Water	22,000
Cooling Water	20,000
Fuels	34,000
Chemicals	15,000
Catalysts	2,000
Total Costs	778,000
Credits	
NH_4NO_3 1,731 T/Y	78,000
H_2SO_4 7,952 T/Y	112,000
Desulfurization Credit	60,000
Total Credits	250,000
Total Annual Operating Costs	528,000
$/Ton NO_x Removed (Calculated as NO_2)	530
mils/KWH	2.01
$/Ton Coal Fired	4.40

* Using 0.7 scaling power factor on 1000 MW plant investment.

APPENDIX 8-50

PLANT INVESTMENT COSTS FOR REMOVING NO_x FROM STACK GAS OF 1000 MW COAL FIRED POWER PLANT USING TYCO'S SULFURIC ACID SCRUBBING CONTROL SYSTEM

Equipment	Material and Labor Costs, $1,000
Cyclones	436
N_2O_3 Mixer	358
Scrubbers	4,900
Filter	293
Stripper (Including Charcoal)	280
HNO_3 Absorber	885
Pumps (Absorber Acid)	218
Pumps (Stripper Acid)	262
Air Blower For Stripper	356
Heat Exchanger for Flue Gas to Stripper	153
Heat Exchanger for Gas to HNO_3 Absorber	1,293
Heat Exchanger for Flue Gas to Absorber	1,252
HNO_3 Acid Storage Tank	380
H_2SO_4 Acid Storage Tank	115
Duct Work	135
Exhaust Fan	621
Material and Labor Sub-Total Costs	11,937
Field Labor Overhead and Burden	2,069
Engineering and Contracting Fees	1,560
Sub-Total for Contingency	15,566
Contingency	2,335
Working Capital	716
Total Plant Investments	18,617
Investment Credits (Elimination of Electrostatic Precipitator)	1,300
Net Investment	17,317

APPENDIX 8-51

ANNUAL CONTROL COSTS FOR REMOVING NO_x FROM STACK GAS OF 1000 MW COAL FIRED POWER PLANTS USING TYCO'S SULFURIC ACID SCRUBBING CONTROL SYSTEM

	Costs $
Capital Charges	2,424,000
Maintenance	866,000
Supplies	130,000
Direct Labor	79,000
Supervision	12,000
Payroll Burden	18,000
Plant Overhead	544,000
Utilities	
Electricity	426,000
Steam	0
Process Water	0
Cooling Water	66,000
Fuels	0
Chemicals	0
Catalysts	48,000
Total Costs	4,613,000

	Scrubber Efficiency, % Removed					
	98		95		92	
Credits						
H_2SO_4 (T/Y)	(173,500)	1,388,000	(168,000)	1,344,000	(163,000)	1,304,000
HNO_3 (T/Y)	(34,700)	1,735,000	(25,250)	1,263,000	(15,685)	784,000
Desulfurization and Operating Credits				1,135,000		
Total Credits		4,258,000		3,742,000		3,223,000
Total Annual Operating Costs		355,000		871,000		1,390,000
$/Ton NO_x Removed (Calculated as NO_2)		14		44		118
mils/KWH		0.06		0.14		0.23
$/Ton Coal Fired		0.17		0.41		0.65

APPENDIX 8-52

PLANT INVESTMENT COSTS FOR REMOVING NO_x FROM STACK GAS OF 1000 MW OIL FIRED POWER PLANT USING TYCO'S SULFURIC ACID SCRUBBING CONTROL SYSTEM

Equipment	Material and Labor Costs, $1,000
N_2O_3 Mixer	358
Scrubbers	4,900
Filter	215
Stripper-Oxidizer (Including Charcoal)	217
HNO_3 Absorber	655
Pumps	360
Air Blower for Stripper	260
Heat Exchanger for Flue Gas to Stripper	115
Heat Exchanger for Gas to HNO_3 Absorber	970
Heat Exchanger for Flue Gas to Absorber	1,252
HNO_3 Storage	380
H_2SO_4 Storage	162
Duct Work	135
Exhaust Fan	621
Material and Labor Sub-Total Costs	10,600
Field Labor Overhead and Burden	1,800
Engineering and Contracting Fees	1,400
Sub-Total for Contingency	13,800
Contingency	2,070
Working Capital	636
Total Plant Investments	16,506
Investment Credits	0
Net Investment	16,506

APPENDIX 8-53

ANNUAL CONTROL COSTS FOR REMOVING NO_x FROM STACK GAS OF 1000 MW OIL FIRED POWER PLANT USING TYCO'S SULFURIC ACID SCRUBBING CONTROL SYSTEM

	Costs $
Capital Charges	2,311,000
Maintenance	825,000
Supplies	124,000
Direct Labor	79,000
Supervision	12,000
Payroll Burden	18,000
Plant Overhead	520,000
Utilities	
Electricity	395,000
Steam	0
Process Water	0
Cooling Water	43,000
Fuels	0
Chemicals	0
Catalysts	32,000
Total Costs	4,359,000

	Scrubber Efficiency, % Removed					
	98		95		92	
Credits						
H_2SO_4 (T/Y)	(109,300)	874,000	(106,000)	848,000	(102,650)	821,000
HNO_3 (T/Y)	(37,360)	1,868,000	(31,620)	1,581,000	(25,870)	1,293,000
Desulfurization and Operating Credits	1,063,000					
Total Credits		3,805,000		3,492,000		3,177,000
Total Annual Operating Costs		554,000		867,000		1,182,000
\$/Ton NO_x Removed (Calculated as NO_2)		20		38		63
mils/KWH		0.09		0.14		0.19

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13. ABSTRACT

This two-volume report presents the findings, conclusions and recommendations of a systems study of nitrogen oxide (NO_x) control methods for stationary sources. The study characterized the nature and magnitude of the stationary NO_x emission problem for the U.S., assessed existing and potential control technology on the basis of nation-wide cost-effectiveness, and recommended a comprehensive 5-year R&D program on stationary NO_x control.

Stationary sources account for 55-60% of the total NO_x emissions in the U.S. between now and the year 2000, estimated on an uncontrolled basis. Fossil fuel sources will be responsible for over 90% of stationary NO_x emissions. Non-combustion sources, e.g., nitric acid plants are important only from the standpoint of local health hazards and aesthetic problems.

Available technology is not well developed for controlling stationary NO_x emissions. Of the potential control techniques assessed, combustion modifications show the most promise because of their relative simplicity and projected low cost. Requirements for the development of a mathematical model predicting the fate of NO_x in combustion processes have been defined and a first-generating model has been formulated in this study.

(Continued)

Abstract (Cont'd.)

Combustion flue gas treatment techniques may need to be developed to control NO_x emissions from large, coal fired electric power plants, since suitable combustion modification techniques may not be feasible for this category of emission sources. Such treatment may also control sulfur oxide and particulate emissions. Technology is available for controlling emissions from plants manufacturing or using nitric acid, but case-by-case economic and engineering evaluations are required to select the most appropriate techniques.

The 5-year R&D plan recommendations made for the National Air Pollution Control Administration are based on the cost-effectiveness of developing stationary NO_x emission control technology and on the knowledge gaps identified in this systems study. These recommendations consist of basic and applied program items, which involve combustion processes, flue gas treatment processes, non-combustion processes and the required support studies. The program items are grouped in priority blocks, based on their potential impact on stationary NO_x emission levels in the U.S.

Volume I of this report contains the summary of the work and the 5-year R&D recommendations. Complete details of the NO_x systems study are presented in Volume II of this report.

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Nitrogen dioxide						
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Sulfur oxides						
Particulates						
Fossil fuels						
Coal						
Fuel oil						
Gas						
Control						
Removal						
Abatement						
Combustion processes						
Flue gases						
Non-combustion processes						
Process modifications						
Operating features						
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Oil and gas industry						
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Thermodynamic equilibrium						
Chemical kinetics						
Mathematical modeling						
Research and development plans						
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